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SOVIET RESEARCH ON SEMICONDUCTOR THIN FILMS: A SURVEY

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10. ABSTRACT

A review of Soviet semiconductor thin film research openly published in four major journals during 1970-1972, plus some earlier reports from other journals--over 200 papers in all. Recent Party directives call for mass production of high performance computers, and hence require major efforts to develop semiconductor thin film technology. Epitaxial growth is stressed particularly. Following a brief history, the report surveys the preparation research and studies of film characteristics: Structure and morphology; electrical, galvanomagnetic, acoustic, and optical properties; quantum size and space effects. Reported measurement techniques are found uninteresting, and little information was available on applications. The Soviet research appears generally to be a few years behind the U.S., but is ahead in work with polymer compounds. Individual research groups appear to be pursuing local interests, with no organized or directed national effort.

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Soviet Research on Semiconductor Thin Films: A Survey

George Rudins

A Report prepared for

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PREFACE

This report has been prepared within the framework of a continuing program, sponsored by the Defense Advanced Research Projects Agency, which undertakes the systematic coverage of selected areas of Soviet scientific and technical literature. It is a preliminary review of the current state of the art in the area of semiconductor thin-film research in the Soviet Union, with particular attention to the more recent developments. The study seeks to provide an overall picture of Soviet activities, interests, and trends in this field, and the approach used, therefore, is general and descriptive. Its chief value, it is hoped, will be as a starting point for the investigation of any special topics that future researchers may select from the broad spectrum presented in this survey.

SUMMARY

The present Report is a preliminary review of current Soviet research in the area of semiconductor thin films. It seeks to provide a general picture of Soviet activities, interests, and trends in this field, and is intended to serve both as a benchmark of current Soviet technology and as a starting point for subsequent in-depth analysis of one or more of the specific topics presented. The study is based on over two hundred recent articles from the open Soviet literature. The published Soviet work leads one to conclude that in semiconductor thin-film technology the USSR is generally a few years behind the United States, with the exception of some narrow aspects of materials in which it is ahead. The Soviet Union's current research program in the area of semiconductor thin films represents a comprehensive approach to the subject. The entire range of thin-film topics -- paralleling Western research -- is evident in the Soviet literature.

The Report is divided into ten sections, each treating a traditional textbook aspect of thin-film research. The first two present an overview of Soviet work, including a brief historical discussion of previous Soviet achievements and research efforts. Section III discusses Soviet work on film deposition. Soviet film preparation techniques do not differ from those in the West. Much of the vacuum deposition work, however, has been carried out at about 10^{-5} torr -- a pressure that would probably be viewed as inadequate by U.S. standards -- but film preparation at pressures as low as 10^{-10} torr has been reported. The epitaxial growth of thin semiconductor films is being stressed particularly. Dominant preparation techniques can be divided into two general

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groups: (1) oriented epitaxial crystallization on monocrystalline substrates, and (2) crystallization on nonoriented substrates. Vacuum techniques appear to be most promising in the epitaxial growth of thin films. Epitaxial films of Si, Ge, and certain semiconductor compounds have been prepared in vacuums of 10^{-10} torr using ion pumps on preheated, oriented monocrystalline substrates. Soviet scientists found they could reduce the required operating vacuum either by decreasing the separation between the vaporizer and the substrate to a fraction of a millimeter or by increasing the density of the sputtered material in the vapor phase using laser or electron beams, pulsed heating, ionic sputtering, or arc discharge. Epitaxial film growth was also accomplished via explosion of metallic and semiconductor wires to achieve a low-temperature plasma ($\sim$200,000° K) with a deposition material density of 10^{18} cm^{-3} in a 10^{-5} torr vacuum.

The bulk of the Report (Sections IV-VIII) surveys studies of various film characteristics -- e.g., structure and morphology, electrical, galvanomagnetic, acoustic, and optical properties, and quantum-size and space effects. Most of the Soviet work centers on semiconductor materials that have been thoroughly researched in the United States. However, current work with polymer compounds -- specifically, polydiphenylacetylene, copolymers at vinylidenfluoride with tetrafluoroethylene, pentacene, tetrathiotetracene, pinacyanol, phtalocyanin, and diphenylpolyene compounds -- appears to be of significant interest.

The remaining two sections of the Report discuss thin-film devices and application (Section IX) and film-measurement techniques (Section X). Soviet measurement techniques were found to be uninteresting, and little information was available on thin-film applications. But Soviet

scientists appear to be entering a phase where they will have to stress the development of thin-film elements.

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I. INTRODUCTION

The Soviet Union's current research program in the area of semiconductor thin films represents a wide-ranging approach to the subject. The entire range of thin-film topics -- paralleling Western research -- is evident in the Soviet literature.

The present survey is by no means exhaustive, but it does represent a thorough coverage of four major Soviet journals -- *Solid State Physics, Semiconductor Physics and Technology, Crystallography, and Doklady of the USSR Academy of Sciences* -- for the 1970-1972 period, supplemented by articles from a dozen other journals covering a longer time period. The determination of whether a given film was thick or thin was based on the actual Soviet classification and not on U.S. standards.

Soviet efforts in this field should be especially interesting during the present five-year plan -- a period during which the USSR is being spurred to improve its electronics industry significantly. Recent Party directives called for accelerating the introduction of scientific innovations into industry, particularly the computer industry.[1] The XXIV Communist Party Congress set the task of "mass production of high-performance computers . . . together with all necessary I/O peripherals and software." To achieve this goal, the USSR must dramatically improve quality control in its electronics industry and must further develop such basic areas as semiconductor electronics -- where thin-film technology

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[1] L. I. Brezhnev, *Report of the Central Committee of the Communist Party of the USSR to the Twenty-Fourth Congress*, Politizdat, Moscow, 1971.

occupies a major role. On this basis, it is quite reasonable to expect the Soviets to make a major effort in the development of semiconductor thin films during 1972-1975. The evidence contained in the literature examined would appear to indicate that Soviet research in this area is already on a substantial scale and may possibly make a greater contribution to Soviet computer technology in the next decade than it has in the past.

Vul and Kudryavtsev[2] have identified five major areas in semiconductor electronics to be stressed by the present Soviet effort:

1. Plasma phenomena
2. Dielectric, acoustic, and optical properties
3. Properties of amorphous semiconductors
4. Superconductivity in semiconductors
5. Synthesis of new semiconducting and dielectric materials

Research in these areas should yield interesting developments. The broad review here undertaken does not, however, permit us to draw definite conclusions as to which of the material discussed is actually new and not simply a rehashing of old material, and it is correspondingly difficult to judge whether the Party's directives are being carried out on the required scale.

Soviet film preparation techniques do not differ from those in the West. Much of the vacuum deposition work has been carried out at about 10^{-5} torr -- a pressure that would probably be viewed as inadequate by U.S. standards -- but film preparation at pressures as low as 10^{-10} torr has been reported. The epitaxial growth of thin semiconductor films is being stressed particularly. Dominant preparation techniques can be

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[2] B. M. Vul and V. A. Kudryavtsev, "Semiconductor Electronics in Scientific and Technological Progress," *Fizika i tekhnika poluprovodnikov*, Vol. 5, No. 11, 1971.

divided into two general groups: (1) oriented epitaxial crystallization on monocrystalline substrates, and (2) crystallization on non-oriented substrates.

Aleksandrov[3] recently discussed some basic aspects and trends of Soviet semiconductor thin-film research. According to him, vacuum techniques appear to be most promising in the epitaxial growth of thin films. Vacuum epitaxy is considered a well-established method, whose success has been hindered by the necessity of not only establishing a free path for atoms from the vaporizer to the substrate but also creating a high atom concentration in the semiconductor being deposited and in the residual gases. Epitaxial films of Si, Ge, and certain semiconductor compounds have been prepared in vacuums of 10^{-10} torr using ion pumps on preheated, oriented monocrystalline substrates.

Soviet scientists found they could reduce the required operating vacuum either by decreasing the separation between the vaporizer and the substrate to a fraction of a millimeter or by increasing the density of the sputtered material in the vapor phase using laser or electron beams, pulsed hearing, ionic sputtering, or arc discharge. According to the same source, epitaxial film growth was also accomplished via explosion of metallic and semiconductor wires to achieve a low-temperature plasma ($\sim$ 200,000° K) with a deposition material density of 10^{18} cm^{-3} in a 10^{-5} torr vacuum.

Drop formation on surfaces of growing semiconductor films was eliminated by lowering of the vaporization time to several μsec. The

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[3] L. N. Aleksandrov, "Preparation and Investigation of Semiconductor Films," *Vestnik AN SSSR*, No. 3, 1972. Information contained in this and the remaining paragraphs in this section was extracted from this article.

preheating of semiconductor wires to lower their resistivity facilitated the preparation of high-melting-point semiconductor films with wide forbidden gaps -- e.g., SiC and carbides of transition or rare-earth metals. And, the Soviets claim to have obtained very thin (~100 Å) films of such semiconductor compounds as InSb exhibiting a relatively high charge-carrier mobility -- previously unattainable -- which led to research on quantum-size effects. The technique for obtaining the InSb films was based on the film recrystallization phenomenon observed in growing films following emission of crystallization heat, and on the fact that the original material retains its stoichiometric composition during deposition.

The Soviets have improved cathodic sputtering in an inert gas atmosphere to the point where they were able to increase pressures to 10^{-4} torr and still obtain Si epitaxy. Cathodic current determined the growth rate and threshold temperature -- the minimum temperature at which growth was observed. Through current manipulations, threshold temperatures were lowered to ~550° C. In the case of thermal deposition, such temperatures could only be achieved at 10^{-10} torr.

Research on the preparation of GaAs films led to the development of a methodology for growing films with charge-carrier mobilities of up to 8000 cm^2/vsec (at room temperature) and impurity concentrations of less than 10^{15} cm^{-3} in an open chloride process using $AsC\ell_3$ as the reagent. These parameters were retained by films up to 5 μ in thickness. Soviet research on structural, mechanical, electrical, and optical properties of semiconductor films in the 20-40 μ range involves techniques developed for macroscopic specimens. As a result, the first properties to be studied are those inherent in semiconductor materials in general.

For thin films, whose thickness approaches the Debye screening distance for a space charge or the length of the charge-carrier free path, classical methods are used to determine the effect of film thickness on exhibited properties. Theoretical studies on size effects (published in 1969) have not yet been fully verified experimentally because of difficulties in obtaining $\sim 10^{-1}$ μ-thick semiconductor films with stable parameters. In still thinner films (100-1000 Å), where the energy spectrum becomes quantized and other unique phenomena appear, the Soviets have not made much progress.

Soviet scientists have published very little on semiconductor thin-film applications. But their research appears to be entering a phase where they will have to stress the development of thin-film elements.

Early applications-oriented research appears to have been concentrated in two institutes -- the Moscow Institute of Steel and Alloys, and the USSR Academy of Sciences' Radio Engineering and Electronics Institute. The Moscow Institute used the empirical approach to develop materials for specific electronic applications. In 1969 it used an improved pyrolytic technique for growing ZnO films on Si, Ge, and GaAs for use in piezoacoustic transducers and delay lines. The technique consisted of thermal decomposition of the preliminarily activated zinc proportionate or acetylacetonate vapor in an inert atmosphere. The growth rate of the film varied with the type and

surface treatment of the substrate used. Oriented ZnO structure was observed in films up to 1 μ thick.[4] The second institute is the source of a 1969 patent for a semiconductor thin-film triode.[5] This institute also showed that the gas transport method facilitates the growth of epitaxial films with sufficient purity for successful use in a variety of devices.[6]

Aleksandrov, in the aforementioned article on "Preparation and Investigation of Semiconductor Films," concludes that the Soviet Union's present thin-film-growth technology is inadequate to meet the need of domestic microelectronics. A major problem area has been controlling the growth of multilayer structures with specific parameters. Gas transport methods of epitaxial growth are not yet sufficiently developed for industrial applications involving multiple-element compounds of the A^3B^5 type. Vacuum methods have not been developed to the point where integrated circuits can be fabricated in a single cycle. And the discrepancy has not been resolved between the enormous scope and quantity of experimental research on film-preparation methods and the small number of theoretical, unifying, and direction-providing studies without which the physics of thin solid films cannot take shape.

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[4] V. F. Korzo et al., "Pyrolytic Growth of ZnO Film in an Inert Atmosphere," *Izvestiya neorganicheskiye materialy AN SSSR*, Vol. 5, No. 2, 1969.

[5] Z. Abbyasov and A. S. Maksimov, "Field Effect Triode," *Otkrytiya, izobreteniya, promyshlennye obraztsy, tovarnye znaki*, No. 31, December 1969.

[6] S. A. Aitkhozin et al., "Electrical Properties of GaAs Epitaxial Films Grown by the Gas Transport Method," *Fizika i tekhnika poluprovodnikov*, Vol. 4, No. 5, 1970.

On the basis of Alexsandrov's statement lamenting the lack of direction in Soviet semiconductor thin-film studies, and given the large number of articles published and the wide range of topics they cover, it would appear that the Soviet effort in this area lacks organization. Individual research groups appear to be concentrating on topics of local interest, irrespective of whether their work contributes to the national effort in this area.

II. EARLY THIN-FILM RESEARCH

Soviet efforts to create thin films of perfect single-crystal structure began in the early 1950s at the Institute of Crystallography in Moscow, where subsequently methods were developed for qualitatively controlling the surface structure of Ge single crystals and films obtained via vacuum deposition on calcium and mica substrates.[1] Early studies concentrated on Ge. For example, G. A. Kurov is credited with the analysis of the causes of imperfections arising in Ge films, the effect of residual oxygen on film structure, and the equilibrium conditions for a growing Ge film.[2] V. D. Vasilyev and A. A. Tikhonova performed electron microscopy studies of vacuum-deposited Ge film structure and obtained more perfect Ge films by increasing saturation levels during the vacuum deposition process. The explanation for the absence of imperfections under the experimental conditions was attempted on the basis of a "seedless" growth process, but was incomplete.[3]

Thin films of various semiconductor compounds have been the subject of a wide range of investigations at the Institute of Crystallography.

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[1] Z. G. Pinsker and S. A. Semiletov, "Investigation of Thin-Film Structure in the USSR," *Kristallografiya*, Vol. 12, No. 5, 1967.

[2] G. A. Kurov, "Imperfections in Ge Films," *Fizika tverdogo tela*, No. 5, 1963; "Equilibrium Conditions for a Growing Ge Film," ibid., No. 4, 1962.

[3] V. D. Vasilyev and A. A. Tikhonova, *Rost kristallov (Sbornik)*, No. 8, Izd-vo AN SSSR, Moscow, 1967.

Long-range electron diffraction investigations[4] revealed that compound dissociation depends mainly on the nature of the chemical bonds, and that semiconductor compounds can be divided into three categories: (1) nondissociating when heated, such as molecular and ionic crystals and semiconductors of the PbS group; (2) dissociating when heated but vaporizing in the solid state, such as crystals with covalent bonds (A^2B^6 group); and (3) dissociating when heated but vaporizing in the liquid state, such as the A^3B^5, and $A_2{}^4B_3{}^6$ groups. Progress in the understanding and handling of each group was outlined. The parameters of the films of the first group have been made to approach those of single crystals.[5] A^3B^5 films -- e.g., epitaxial films of InSb, InAs, and GaSb -- were obtained by flash evaporation.[6] Here the divergence from single-crystal characteristics consisted of a sharp drop in electron mobility (in InSb) as the temperature was lowered to the liquid-nitrogen levels (the gradient of the drop depended on the concentration of electrons). The phenomenon was attributed to an excess (up to 40%) of indium in the

[4] Z. G. Pinsker, "Electronographic Investigation of Crystals," *Zhurnal strukturnoy khimii*, No. 1, 1960; and S. A. Semiletov, V. A. Vlasov and Z. A. Magomedov, Reports of the VIIth International Congress on Crystallography, Moscow, 1966.

[5] S. A. Semiletov, I. P. Voronina, and E. I. Kortukova, "Nondissociating Semiconductor Compounds," *Kristallografiya*, No. 10, 1965.

[6] S. A. Semiletov, P. S. Agalarzade, and E. I. Kortukova, "Flash Evaporation of A^3B^5 Epitaxial Films," *Kristallografiya*, No. 10, 1965.

film. Notwithstanding their structural imperfections, such films were found to be suitable for devices such as Hall transducers, magnetic resistors, and thin-film transistors.[7] A^2B^6 compounds, which have the formation characteristics of two-phase films (first established by Semiletov[8]) with a large number of packing defects, were first observed in electron diffraction studies of CdTe, CdS, and CdSe films. Analysis of these compounds led to the discovery of the existence of continuous change from one structure to another and of the existence of microcrystals with alternating structure, resulting in a better understanding of the high-voltage photoelectric effect in CdTe films.[9] U.S. researchers, J. de Klerk and E. F. Kelly[10] later demonstrated that these films can be used as piezoelectric transducers of hypersonic (10^6 - 10^6 cps) oscillations. Thin-film Hall transducers based on HgSe and HgTe were first produced by Yelpatyevskaya and Regel and were used for measurement of magnetic fields in narrow gaps.[11]

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[7] T. P. Brady and H. E. Kunig, "Applications of A^3B^5 Films," *Applied Physics Letters*, No. 9, 1966.

[8] S. A. Semiletov, "A^2B^6 Two-Phase Films," *Trudy Instituta kristallografii AN SSSR*, No. 11, 1955.

[9] S. A. Semiletov, "High-Voltage Photoelectric Effect in CdTe Film," *Fizika tverdogo tela*, No. 4, 1962.

[10] J. de Klerk and E. F. Kelly, "Piezoelectric Transducers of Hypersonic Oscillations," *Review of Scientific Instrumentation*, No. 36, 1965.

[11] O. D. Yelpatyevskaya and A. R. Regel, "Thin-Film Transducers," *Zhurnal tekhnicheskoy fiziki*, No. 1, 1956.

Thin-film production by chemical reactions was investigated for Ge, Si, and GaAs.[12] Two crystallization regions were established for Ge and Si -- a low-temperature region (with an atomic growth mechanism) and a high-temperature region (with a droplet mechanism).[13] Givargizov and Stepanova[14] developed a method of gas-etching the substrate surface to eliminate dislocations in the transition layer. The effects of mass transfer (convection, gas flow, etc.) were experimentally studied by Kurov,[15] with the conclusion that the heterogeneity of the disproportioning reactions in which the substrate acts as a catalyst must be the main cause of imperfections. The iodide method of formation of Ge films was studied with respect to the effects of mass transfer.[16] The best films were obtained when the surface of the substrate was shielded from gas currents by a plate which was both close and parallel to the substrate. Ya. Kh. Grinberg and others succeeded in growing single crystals of boron phosphide by chemical transport reactions.

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[12] N. N. Sheftal and N. P. Kokorish, *Rost kristallov (Sbornik)*, No. 4, Izd-vo AN SSSR, Moscow, 1964.

[13] N. N. Sheftal, E. I. Givargizov, B. V. Spitsyn, and A. M. Kevorkov, *Rost kristallov (Sbornik)*, No. 4, Izd-vo AN SSSR, Moscow, 1964; N. N. Sheftal and E. I. Givargizov, ibid., No. 8, 1967.

[14] E. I. Givargizov and A. N. Stepanova, "Elimination of Dislocation in the Transition Layer," *Kristallografiya*, No. 9, 1964.

[15] G. A. Kurov, "Effects of Mass Transfer in Substrates," *Fizika tverdogo tela*, No. 5, 1963.

[16] V. F. Dorfman, K. A. Bolshakov, and I. P. Kislyakov, "Iodide Method of Ge Film Formation," *Izvestiya AN SSSR, Seriya neorganicheskie materialy*, No. 1, 1965.

The characteristics and shortcomings of electron diffraction techniques based on diffraction by single-crystal mosaics and the multiwave scattering from near-perfect single-crystals over 1000 Å thick wave investigated. Kikuchi lines, whose relationship to the structural characteristic was not clearly defined, were used to a limited extent for the qualitative testing of the surface of the film, as reflected in the sharpness of the line profiles. Kikuchi lines were also used for orienting specimens in electron microscopy investigations. With the discovery of the geometry and distribution of intensity in the basic imperfections, electron diffraction microscopy became an important research tool.[17] The study of etching effects via electron microscopy was considered promising.[18]

In the early sixties, several papers appeared which suggested a revision in the fundamentals of existing electron diffraction methods for investigating atomic structures of thin films. The Soviets also found that the Vaynshteyn criterion, even though it tends toward overestimation, was still valid if a predominantly kinematic scattering in the usual layer thicknesses was assumed. Inelastic scattering as a factor affecting the pattern intensity proved to be of no great consequence in the interpretation of experimental data.

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[17] Z. G. Pinsker and S. A. Semiletov, "Investigational Thin-Film Structure in the USSR, *Kristallografiya*, Vol. 12, No. 5, 1967.

[18] V. D. Vasilyev and A. A. Tikhonova, *Rost kristallov (Sbornik)*, No. 8, Izd-vo AN SSSR, Moscow, 1967.

The atomic structure of two-, three-, and, to a certain extent, four- component semiconductor compounds has been under investigation for the past twenty years, and metastable compounds have been discovered -- e.g., CdS, CdSe, CdTe, and InSb films[19]-- along with some entirely new compounds -- e.g., Bi-Se and Bi-Te film systems.[20] Pinkser and Semiletov, in association with others, are also credited with the determination of the structure of a number of semiconductor compounds ($T\ell SbSw_2$, InSe, In_2Se_3, a number of Ag and Bi compounds, etc.), the results of which changed materially the earlier ideas about certain problems of semiconductor composition and structure. Structure determination of compound lattices with over 50 atoms in a unit cell (Ag_7Te_4, K_2SO_4, $Cs_2CoC\ell_4$, etc.) became possible through further development of electron diffraction methods.[21] The method of kinematic electron diffraction was considered promising for the investigation of phase transitions in films.[22] Isothermal mapping was also widely used. In

[19] S. A. Semiletov, "Metastable Phases in Semiconductors," *Kristallografiya*, No. 1, 1956; and "Multicomponent Semiconductor Phases," ibid., No. 2, 1957.

[20] S. A. Semiletov, "Semiconductor Phases in Bi-Se and Bi-Te Film Systems," *Trudy Instituta kristallografii*, No. 10, 1954.

[21] R. V. Baranova and Z. G. Pinsker, "Determination of Compound Lattice Structure," *Kristallografiya*, No. 10, 1965; V. V. Udalova and Z. G. Pinsker, "Electronographic Method in Structure Determination," ibid., No. 8, 1963; R. V. Tishchenko and Z. G. Pinsker, "Electronographic Analysis of Compound Lattices," *Doklady AN SSSR*, No. 100, 1955.

[22] G. A. Efendiyev, doctoral dissertation, Azerbaidzhan State University, Baku, 1966.

these methods, the diffraction pattern on a movable plate revealed the process of formation of equilibrium states in a multicompound system. Important regularities of the process were established by this method. Electron diffraction was also applied to investigations of amorphous substances, such as amorphous antimony and certain compounds.[23] L'vov University is engaged in a methodological work, while Khar'kov University is concentrating on liquid alloys. The electron diffraction method has proved successful in the structural analysis of synthetic polypeptides.[24]

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[23] L. I. Totarinova, "Electronographic Investigation of Amorphous Substances," *Kristallografiya*, No. 1, 1956.

[24] B. K. Vaynshteyn and L. I. Totarinova, *Symposium on Biopolymer Compounds*, Madras, 1967.

III. PREPARATION OF THIN FILMS

DEPOSITION VIA ELECTRIC WIRE EXPLOSION

The Institute of Semiconductor Physics of the Siberian Branch of the USSR Academy of Sciences has apparently been doing considerable work on the deposition of thin films via electric wire explosion. The work involved depositing InSb and InAs films onto isolated nonoriented substrates.[1] The films were about 100 Å thick, and the deposition rate varied from about 1 to 10 cm/sec. The condensing plasma had a very high specific energy ($E_{sp} \sim 10\text{-}10^2$ J/mg and $T \sim 10^5\text{-}10^6$° K).

Despite the observed higher reactivity of the condensed atoms, the absorption of residual gases during the condensation process was found to be insignificant. Obtained molecular-beam densities were greater than those attainable by conventional techniques -- i.e., vacuum evaporation or sputtering. With the aid of an electrostatic probe to measure changes in potential, the Soviets calculated the beam density to be

$$v_s = \frac{\rho_o R_o^2 U_o}{m_s R_k^2 \left(1 + \frac{U_o}{R_k} \Delta t\right)^3} \approx 10^{23} \text{ atoms/cm}^2 \text{ sec},$$

where R_k (the distance between the substrate and the exploding wire) was 7 cm; Δt (condensation time) was ≈ 20 μsec; U_o (plasma expansion velocity) was ~ 10^5 cm/sec; m_s (atomic weight of the condensing materials) averaged about 100 for Ge, InSb, and InAs; ρ_o (density of

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[1] L. N. Aleksandrov, E. I. Dagman, V. I. Zelevinskaya, V. I. Petrosyan, and P. A. Skripkina, "Formation and Properties of Semiconductor Films Obtained Via Electrical Explosion," *Thin Solid Films*, No. 5, 1970.

condensing materials) was ~ $5 g/cm^3$; and R_o (radius of the exploding cylindrical sample) was 0.05 mm. The relative concentration of residual gas impurities in the film was found to be:

$$n_g = \frac{v_g}{v_s} = \frac{P_g}{v_s (2\pi m_g k T_g)^{\frac{1}{2}}} \simeq 10^{-8},$$

where v_g is the rate of arrival of atoms of residual gases at the substrate; k is the Boltzmann constant; P_g is the pressure of residual gases ($\sim 10^{-5}$ torr); T_g is the temperature of residual gases (~ 300° K); and m_g is the atomic weight of residual gases (for air ~ 30). Time dependence and temperature distribution in the growing film and substrate were obtained by a numerical solution of the generalized equation of thermal conductivity with its boundary moving with velocity v due to film growth:

$$\frac{1}{x}\frac{\partial T}{\partial t} = \frac{\partial^2 T}{\partial x^2} - \frac{v \partial T}{k \partial x},$$

where k represents the temperature coefficient of conductivity, assuming that the thermodynamic properties of the film and substrate are equal (taking into account reevaporation and heat exchange via radiation at the boundaries).

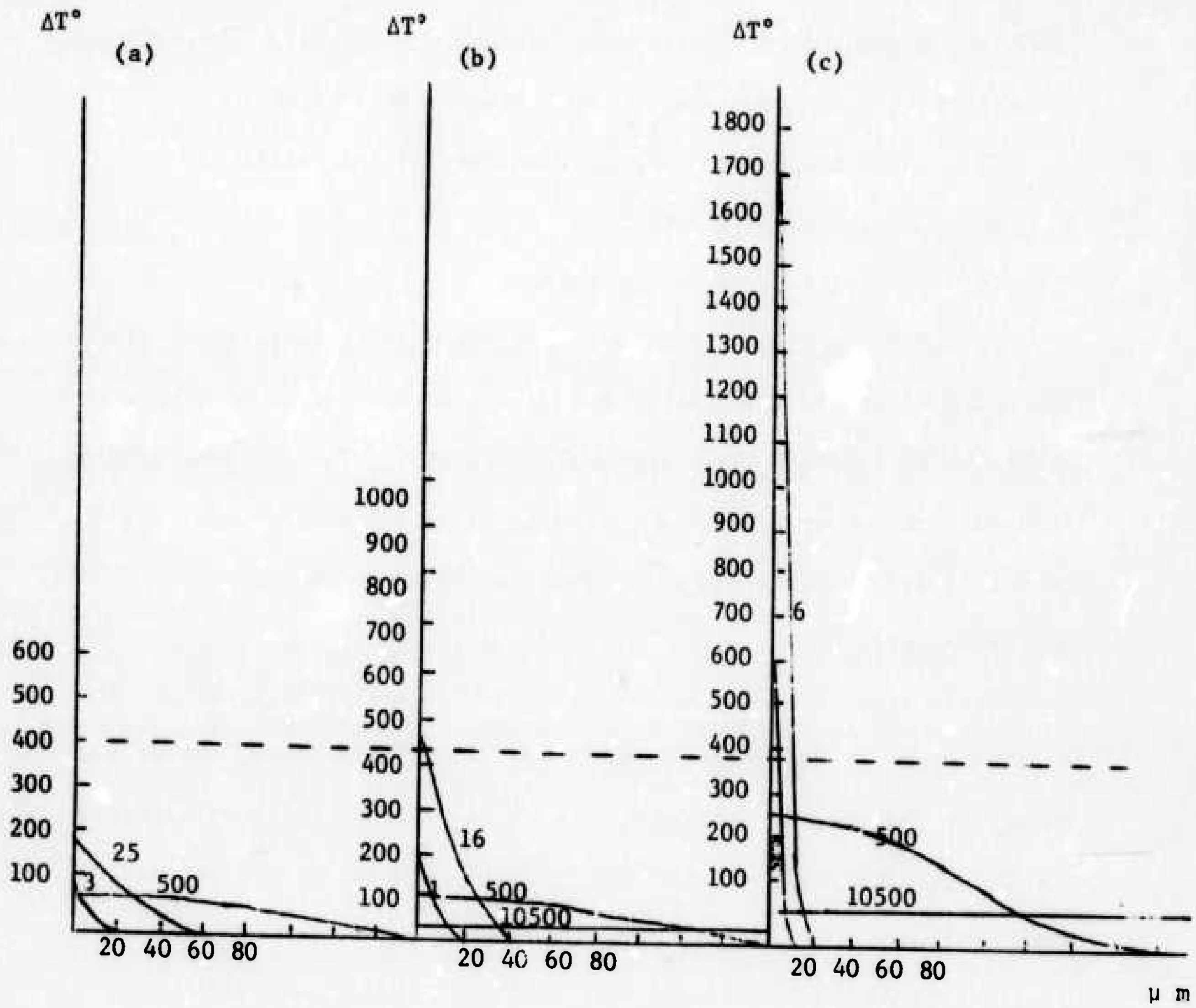

Fig. 1 -- Temperature distribution in a film-substrate system at varying distances from the exploding wire.

(a) R_k = 10 cm; (b) R_k = 5 cm; (c) R_k = 2 cm. Figures on the curves denote the time in μsec from the beginning of condensation. The dotted line corresponds to the melting point of InSb (substrate temperature = 150° C).

It was found that the exploding-wire method produces immediate condensation of high-temperature plasma with fixed explosion energy, and that, depending on the distance between the explosion and substrate, crystallization may occur in one of three possible ways:

(1) at a temperature higher than the melting point;

(2) at the melting point;

(3) with intensive reevaporation.

Figure 1 (a), (b), (c) illustrates examples of temperature distribution in the film and substrate at successive points in time with different distances R_k from the exploded sample. The abscissa reading is made from the surface of the growing film in the direction of the substrate and the ordinate represents temperature rise above the initial substrate temperature.

Three types of films -- Ge, InSb, and InAs -- were studied. The typical size of the exploded sample was 0.1 x 0.1 x 30 mm, the stored energy in the discharge capacitor was 1 kj, the discharge voltage was 500 kv, the discharge current was ~ 150 ka, and the discharge period was ~ 0.2 μsec. Epitaxial films of Ge on Ge and Ge on NaCℓ were of single-crystal structure; however, their electrical properties were difficult to determine because of the high general resistance of the films.

InSb and InAs films deposited on isolated nonoriented substrates of glass and quartz at temperatures near 300° C had a polycrystalline structure with grain sizes of several thousand angstroms. Electron diffraction studies revealed that the stoichiometric composition of the initial compound in the films was maintained.

Electrophysical parameters of the films were determined (at ~ 300° K) from Hall measurements by conventional methods and gave the following:

InSb: n-type, specific conductivity $\sigma \sim 1$ (ohm cm)$^{-1}$, carrier concentration $n \approx 10^{18}$ cm^{-3}, mobility $\mu \sim 10^{2}$ cm^{2} v^{-1} sec^{-1} (compared with the properties of original crystals: n-type, $\sigma = 600$ (ohm cm)$^{-1}$, $n \approx 10^{17}$ cm^{-3}, $\mu \approx 38{,}000$ cm^{2} v^{-1} sec^{-1}).

InAs: n-type, specific conductivity $\sigma \sim 10^{-2}$ (ohm cm)$^{-1}$, carrier concentration $n \approx 10^{19}$ cm^{-3}, mobility $\mu \sim 10^{2}$ cm^{2} v^{-1} sec^{-1} (compared with the properties of original crystals: p-type, $\sigma \approx 180$ (ohm cm)$^{-1}$, $n \approx 8 \times 10^{18}$ cm^{-3}, $\mu \approx 130$ cm^{2} v^{-1} sec^{-1}). Low mobility was explained by dimensional effects in thin films, and was in agreement with results obtained in experiments involving InSb films of 400 Å deposited via flash evaporation (where $\mu \approx 60$-70 cm^{2} v^{-1} sec^{-1}).

On the basis of these experiments, the Soviets drew the following conclusions on the use of electrical explosion in film preparation:

1. The condensation time of films of ~ 10^{2} Å is several tens of μsec with a molecular-beam density of about 10^{23} atoms cm^{-2} sec^{-1}.

2. Depending on the distance between the exploding sample and substrate, crystallization may take place at a higher but not a lower temperature than that of melting, or from the melt, or with intensive reevaporation.

3. Epitaxial growth of thin films (~ 10^{2} Å) is possible under conditions of high supersaturation. The decrease of mobility of thin films obtained in comparison with the bulk values may be explained by dimensional effects.

4. The technique can be used for multiple-deposition of films, since reevaporation can be controlled (see Fig. 1a).

5. Because of high supersaturation in the initial stages of nucleation, the nuclei consist of single atoms. As a result, film formation at low supersaturation occurs via a continuous liquid layer and not by single drops.

GAS-FLOW DEPOSITION

Aleksandrov[2] has been preparing thin semiconductor, dielectric, and metallic films via hydrolysis of metal chlorides and decomposition of metal hydrides (and other compounds) on heated glass substrates. The Soviet gas-flow method -- a variation of the technique for obtaining films from the vapor phase -- is basically film deposition onto a substrate placed into the path of a stream of gas (fed through an appropriate nozzle). When the desired substrate temperature (120-500° C, depending on the film material used) is reached, the gas -- air saturated with the desired metal compound vapors -- is applied to the substrate. The gas-flow rate is determined empirically. The film thickness is a function of the rate of movement of the gas stream across the substrate, the gas-flow rate, the distance from the gas nozzle to the substrate surface, the temperature of the substrate and the gas, and the number of passes across the substrate.

The Soviets have employed the following three chemical reactions in gas-flow deposition:

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[2] This section is based on G. A. Aleksandrov, "Gas-Flow Method of Thin-Film Preparation," *Optiko-mekhanicheskaya promyshlennost'*, No. 2, 1969.

1. Hydrolysis of selected metal chlorides -- $TiCl_4$, $SiCl_4$, $SnCl_4$, and $SbCl_5$ -- using the following reactions:

$$MeC\ell_n + nH_2O \rightarrow Me(OH)_n + nHC\ell$$

$$Me(OH)_n \rightarrow MeO_{n/2} + n/2\ H_2O;$$

2. Decomposition of metal-organic material compounds together with the formation of a metal oxide:

$$Me(OR)_n \rightarrow MeO + CO_2 + H_2O,$$

where R is a hydrocarbon radical;

3. Thermal decomposition of metal hydrides and metal-organic material compounds resulting in the formation of a metal:

$$GeH_4 \rightarrow Ge + 2\ H_2.$$

Homogeneous films of TiO_2, SiO_2, SnO_2, Sb_2O_3 and Ge were obtained.

It was found that films of up to 1 μ thick can be deposited on polished substrates; films of greater thickness than 1 μ exhibited cracking and peeling. The >/μ films exhibited good adhesion to polished glass substrates. The only limitation of this technique is that the compound used must be volatile enough to be satisfactorily dissociated or formed into the desired film material at a temperature that can be tolerated by the substrate. The film thickness can be made either uniform or variable on either flat or spherical surfaces. The technique has been applied mainly to the coating of optical elements.

ELEMENTAL SEMICONDUCTORS

Meshcheryakov recently reported[3] on the effect of shock waves incident on a growing silicon film. He investigated chemical vapor deposition of Si and SiO_2 inside a shock tube. Measurements of the film-growth kinetics, made with the use of a Jamin interferometer and a high-speed camera, showed that Si layers formed within 100-150 μsec SiO_2 layers required 100-300 μsec. When monocrystalline silicon was compressed by shock waves, it developed film imperfections (in specific pressure and temperature ranges), which caused a rearrangement of its energy levels accompanied by a shift of its absorption line toward the infrared region. The study revealed the growth rate of Si and SiO_2 films to be a function of the orientation of the monocrystalline silicon surface used for the substrates.

Zorin and others[4] are investigating nitrogen's role in the formation of inverse layers of p-silicon when the latter is bombarded by ions of inert gases (sputtering) followed by annealing. When p-silicon is exposed to nitrogen ions and then annealed at temperatures $\geq$ 600° C, an inverse layer forms at the surface. Similar inverse layers likewise form when the bombarding ions are of an inert gas. Zorin's paper experimentally explains the mechanism involved in the formation of inverse layers by inert gases on the basis of the electrically neutral nitrogen (in the form of N_2 or Si_xN_y molecules) that is present in the p-silicon being activated by the inert gas ions.

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[3] N. A. Meshcheryakov, "Incidence of a Shock Wave on a Silicon Surface During Thin-Film Formation," *Fizika i tekhnika poluprovodnikov*, Vol. 4, No. 12, 1970.

[4] E. I. Zorin, P. V. Pavlov, D. I. Tetelbaum, and A. F. Khokhlov, "Role of Nitrogen in the Formation of Inverse Layers of p-Silicon when Bombarded by Ions of Inert Gases with Subsequent Annealing," ibid.

Although silicon epitaxy is not usually considered a thin-film process, it is being included in the survey because most epitaxial silicon films are much less then 5 μ thick, and fall within the physical classification of thin films. If the film is polycrystalline, as it is on SiO_2, then the growth process is unquestionably a thin-film process.

W. J. Riedl has done considerable work on epitaxial silicon films.[5] He has demonstrated that the quality of such films hinges on the purity of the silicon seed surface. Contamination of the seed surface with such impurities as Si_3N_4 and SiO_2 can generate imperfections in the deposited epitaxial silicon, and therefore etching of the silicon seed with $HC\ell$ or H_2) vapor (diluted with hydrogen) is necessary. He has investigated the stability and instability of Si_3N_4 and SiO_2 on the silicon surface at various temperatures and partial pressure of N_2, $HC\ell$, and H_2O in H_2, and confirmed that the decomposition of Si_3N_4 by etching in $HC\ell + H_2$ is less effective than in $H_2O + H_2$ mixtures. At a given partial pressure of N_2 in H_2 during H_2O etching, five regions of stability and instability of the aforementioned solid impurities exist in the system of coordinates log pH_2O versus T^{-1}. Further etching conditions given by points within only one region can result in the elimination of both impurities.

In one of his studies on epitaxial silicon films Riedl showed that by using two concepts -- nuclei activity and metastable equilibrium constant -- it is possible to compute conditions under which highly

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[5] W. J. Riedl, "Equilibria Gas-Silicon Nuclei During Deposition of Epitaxial Silicon Films from $SiC\ell_4 + H_2$ Mixtures," and "Instability of SiO_2 and Si_3N_4 on Silicon Surface During Etching of Silicon Substrates Prior to Epitaxial Growth," *Proceedings of the Second Colloquium on Thin Films*, Akademiai Kiado, Budapest, 1968.

active nuclei with deteriorating crystal perfection are unstable and can be eliminated from a system. His work was motivated by the fact that the thermodynamic approach to the deposition of epitaxial silicon from $SiC\ell_4 + H_2$ mixtures neglected nucleation phenomena. He found that in the case of low $SiC\ell_4$ concentrations (usually applied to epitaxial silicon during growth in flow systems), the back transport of silicon from the substrate surface occurs mainly in the form of gases other than $SiC\ell_4$ -- supposedly in contrast to the findings of other researchers. He also showed that, by varying temperature and supersaturation, silicon condensation can be made to occur in two formats -- gas → crystal nuclei and gas → liquid nuclei.

Gavrilov recently made a study of the movement of liquid drops observed on the surface of a growing Ge film.[6] Microscopic examination of Ge deposition (via hydrogen reduction of germanium tetrachloride) in a reactor with a controlled gas flow parallel to the substrate revealed moving droplets which left "tracks" of smooth crystallized steps rising above the surrounding film. The author concluded that the "tracks" were an indicator of rapid growth but did not in themselves contribute to film growth.

Tikhonova[7] measured oxygen content in epitaxial germanium films obtained by vacuum evaporation on a (111) substrate and found very weak desorption of oxygen. The oxygen's coefficient of adhesion to the

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[6] G. M. Gavrilov, "Moving Liquid Drops on the Surface of a Ge Film During Its Growth," *Kristallografiya*, Vol. 16, No. 4, 1971.

[7] A. A. Tikhonova, "Effect of Oxygen on a Growing Germanium Film," ibid.

surface of the growing film was close to one, which exceeded by two orders of magnitude the coefficient of adhesion for a regular crystal face at the same temperatures (700-750° C) and pressure (5×10^{-8} torr). The film's growth rate was about .15 microns/sec. The discrepancy in adhesion was attributed to the microscopic roughness on the growing face and absence of a regular surface. Reduction of the residual gas pressure under various conditions of film formation did not affect the surface morphology but, as with preliminary substrate annealing, did lead to a reduction in the density of imperfections in the growing film. All imperfections appeared in close proximity to the film-substrate interface. Increases in vacuum pressure likewise led to a reduction in imperfections. However, in both cases the imperfections could not be totally removed -- e.g., Ge films prepared in a 1×10^{-9} torr vacuum without preliminary substrate annealing and with condensation temperatures of 850° C and 550-600° C had respective imperfection densities of $\sim 10^4$ and 2×10^6 cm^{-2} (no differences were distinguishable between films formed at 1×10^{-9} torr and those at 3×10^{-7} torr, while identical films prepared in a 5×10^{-6} torr vacuum had imperfection densities of 2×10^5 and 5×10^7 cm^{-2} (substrates were prepared in standard fashion).

Lavrenteva and others[8] investigated both the anisotropy of the growth rate and the anisotropy of epitaxial Ge film-doping oriented between (110)-(100). The films were grown in a vapor-transport system on substrates of Ge and GaAs.

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[8] L. G. Lavrenteva, I. S. Zakharov, and Yu. M. Rumyantsev, "Anisotropy of the Growth Rate and Doping Level During the Epitaxy of Germanium on GaAs Substrates," *Kristallografiya*, Vol. 16, No. 2, 1971.

Belyy and Kuznetsov[9] have worked on the chemical etching of Ge single-crystals to yield a fine-grained film. The transport reactions used by the researchers -- $Ge + 2HBr \rightarrow GeBr_2 + H_2$ and $GeBr_2 + HB_r \rightarrow GeHBr_3$ -- are not new, but (according to the authors) their dependence on temperature is new. At room temperature, no reaction was detected. In the range of 350-500° C the Ge surface was covered by a black velvet-like deposit. Above 700° C a very rapid reaction occurred, yielding a smooth, bright Ge surface. At moderately high temperatures, a rough (but not black) surface developed. The occurrence of a layer-like formation as a result of decomposition was interpreted by the authors in two different ways: (1) The layer was part of the original crystal lattice not destroyed chemically; and (2) the surface regained a portion of the previously etched material via a secondary chemical reaction -- e.g., a disproportionation. The study concentrated on the low-temperature range of the Ge-HBr reaction, where the film was continuous and easily separable from its substrate.

Szep[10] reported experimental work on eutectic AℓGe layers prepared by surface-alloying of thin, small-area aluminum films with germanium. He discussed the role of crystallographic orientation, structural imperfections, and temperature gradients, stressing the importance of surface conditions generated by preliminary treatment or by ambient influence. The observations were interpreted as arising

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[9] V. I. Belyy, F. A. Kuznetsov, and J. Pfeifer, "Chemical Etching of a Ge Monocrystal Producing a Characteristic Fine-Grained Layer," *Proceedings of the Second Colloquium on Thin Films*, Akademiai Kiado, Budapest, 1968.

[10] I. C. Szep, "Some Observations During the Alloying of Thin Aluminum Films into Germanium," ibid.

from the interactions of surface and bulk forces -- i.e., interfacial tension and dissolution potential versus bond strength on different atomic planes.

EPITAXIAL GaAs

Kulish[11] recently calculated the growth rate of semiconductor epitaxial films (particularly In-Ge and Ga-GaAs systems) from a force-cooled solution. A model of multilayer, two-dimensional film growth is the basis for most of the computations. Kulish found that the major parameters determining the film's electrical and structural properties were the rate of dissolution and growth level of doping of the film and substrate, type of doping material, and mode of epitaxy. The purpose of the study was to produce epitaxial semiconductor films with specific properties through the study of the growth mechanism and the effect of epitaxy conditions on film characteristics. Statistics were derived, showing the effective film-growth rate and rates of nucleus formation and growth as a function of temperature.

EPITAXIAL A^2B^6 COMPOUNDS

Semiletov and Rabadanov[12] have prepared epitaxial ZnO films on monocrystalline semiconductors (Ge and GaAs) with the following orientation:

1. (0001) ZnO || (111) Ge, GaAs
2. $(10\bar{1}3)$ ZnO || (110) Ge, GaAs
3. $(10\bar{1}2)$ ZnO || (100) Ge, GaAs

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[11] V. M. Kulish, "Calculation of the Growth Rate of Semiconductor Films Obtained by Epitaxy from Liquid Metal Solutions," *Izvestiya vysshikh uchebnykh zavedeniy, fizika*, No. 12, 1972.

[12] S. A. Semiletov and R. A. Rabadanov, "Epitaxial ZnO Layers on Ge and GaAs," *Kristallografiya*, No. 2, 1972.

In all three cases, the ZnO crystal lattice $[10\bar{1}0]$ was arranged so that its direction was parallel to that of the [110] Ge and GaAs. The stated purpose of this study was to examine materials of potential use as acoustic amplifiers. The same authors also examined the micromorphology and peculiarities of the growth of ZnO films on mica.[13]

Kotelyanskiy and others[14] have investigated the epitaxial growth and behavior of CdS films on GaP on the basis of slow electron diffraction. The heteroepitaxial CdS films (hexagonal and cubic) were grown on the (111) and $(\overline{111})$ surfaces of GaP in the presence of hydrogen using vapor-transport reactions. The film structure was studied in the temperature interval of 290-900° K.

Vanyukov and others[15] have shown that the optimal conditions for proper epitaxial growth of any A^2B^6 compound are predictable if the ideal growth conditions for any single compound in this category are known. To prove their point, they analyzed several compounds -- e.g., $CdTe-H_2$, CdTe-Ar, $ZnTe-H_2$, and $CdS-H_2$.

Magomedov and Sheftal[16] have examined the potential uses of single-crystal ZnTe films (on a GaAs substrate) obtained from the vapor phase (particularly in optical devices). They argue that the prime

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[13] R. A. Rabadanov and S. A. Semiletov, "Micromorphology and Peculiarities of the Growth of Epitaxial Zinc Oxide Films on Mica," *Kristallografiya*, Vol. 16, No. 5, 1971.

[14] I. M. Kotelyanskiy, A. Yu. Mityagin, and V. P. Orlov," Epitaxial Growth of CdS on GaP with the Aid of Slow Electron Diffraction," ibid.

[15] A. V. Vanyukov, I. I. Krotov, and N. G. Mnatsakanyan, "Approximation Method for Evaluating Conditions for Obtaining Epitaxial Films of A^2B^6 Compounds," *Neorganicheskiye materialy*, Vol. 8, No. 4, 1972.

[16] N. N. Magomedov and N. N. Sheftal, "Preparation of Zinc Telluride Monocrystalline Films from the Gas Phase," *Neorganicheskiye materialy*, Vol. 8, No. 2, 1972.

determinants of a film's electrical properties and purity are growth conditions and, to a lesser extent, the type of substrate used.

Blinnikov and Kalyuzhnaya[17] have grown single-crystal films of CdS via liquid epitaxy. They claim that growth from the liquid phase is more easily controllable than that from the vapor phase and that, as a result, the grown films are much more perfect. Their technique is applicable to all A^2B^6 compounds.

Ratcheva-Stambolieva and others[18] are working on the oriented growth of CdS and CdSe epitaxial films on (111) Ge and (111) CaF_2 substrates in a hydrogen atmosphere. The authors claim they realized single-phase monocrystalline films of CdS and CdTe with a more perfect structure and better defined properties via their method (using transport reactions or sublimation) than is usually possible through vapor evaporation techniques, where it is critical to maintain growth conditions close to equilibrium..

Vanyukov and Krotov[19] are also working on the epitaxial growth of A^2B^6 films from the vapor phase, particularly the growth of cadmium telluride on a CaF_2 substrate.

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[17] G. A. Blinnikov and G. A. Kalyuzhnaya, "Conditions for CdS Crystallization by Liquid Epitaxy," *Neorganicheskiye materialy*, Vol. 8, No. 4, 1972.

[18] T. Ratcheva-Stambolieva, Yu. D. Chistyakov, D. H. Djoglev, and V. S. Bakardieva, "Production of CdS and CdSe Epitaxial Layers from the Vapor Phase," *Physica Status Solidi*, No. 10, 1972.

[19] A. V. Vanyukov and I. I. Krotov, "Epitaxial Growth of Cadmium Telluride on CaF_2," *Kristallografiya*, Vol. 16, No. 3, 1971.

EPITAXIAL A^4B^6 COMPOUNDS

Vlasov and Distler[20] have used vacuum evaporation to study the growth of epitaxial films of AgCℓ and PbS. They have examined the effect of lack of orientation in the initial nuclei during the growth process.

Distler and others[21] maintain that the formation and growth of nuclei at early crystallization stages essentially determine the structure and properties of thin single-crystal films. They studied the early crystallization stages of lead sulphide on single-crystal substrates -- cleavage surfaces of mica and NaCℓ crystals -- using electron microscopy and electron diffraction. Deposition of the PbS was by means of chemical crystallization from solutions and via vacuum evaporation (10^{-6} torr pressure). The scientists detected the presence of active centers initiating oriented nucleation and positioned both on steps and on the smooth regions of the crystal surface. They obtained a continuous single-crystal film of PbS on the outer side of an amorphous carbon layer deposited on the surface of an NaCℓ single-crystal.

Czapla and others[22] obtained thin films of lead oxides by reactive cathode-sputtering in an argon-oxygen mixture. Sputtering -- executed in a 96% Ar + 4% Oz atmosphere -- yielded PbO films of tetragonal and orthorhombic structure and PbO solid solutions of pseudocubic structure.

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[20] V. P. Vlasov and G. I. Distler, "Absence of Orientation in the Initial Nuclei During the Epitaxial Growth of AgCℓ and PbS," *Kristallografiya*, ibid.

[21] G. I. Distler, S. A. Kobzareva, and Y. M. Gerasimov, "Formation of Thin Films of Lead Sulphide on Monocrystalline Substrates," *Proceedings of the Second Colloquium on Thin Films*, Akademiai, Kiado, Budapest, 1968.

[22] A. Czapla, M. Jachimowski, and E. Kusior, "Obtaining Thin Films of Lead Oxides by Reactive Cathodic Sputtering," *Acta Physica Polonica*, Vol. 41, No. 2, 1972.

They examined the effect of sputtering conditions -- e.g., pressure, power, and substrate-cathode distance -- on the structure of grown films and found that certain selected conditions of film formation allow a pure orthorhombic or a pure tetragonal phase to be achieved.

EPITAXIAL GROWTH

Distler[23] is doing considerable work on the formation mechanism of single-crystal films on appropriate single-crystal substrates (epitaxy and autoepitaxy). In this connection, he discusses the mechanism of oriented nucleation based on the existence of local active centers (on crystal surfaces) which are structural defects. The local active centers differ in activation energy for nucleation, orientation effect, and extent of long-range influence.

Aleksandrov and Sidorov[24] have examined the diffusion processes involved in the growth of epitaxial films. They have argued that the formation of epitaxial films is connected with the execution of transport processes involved in the deposition of films from the vapor phase and with surface processes on the substrate. However, their main consideration has been the limiting processes in film growth.

Lyubov and Plakhotnik[25] have computed the impurity distribution in an epitaxial film as a function of film thickness varying with

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[23] G. I. Distler, "Real Structure of Crystalline Surfaces and the Mechanism of Thin Film Formation," *Proceedings of the Second Colloquium on Thin Films*, Akademiai Kiado, Budapest, 1968.

[24] L. N. Aleksandrov and Yu. G. Sidorov, "On the Diffusion Processes During the Growth of Epitaxial Films," ibid.

[25] B. Ya. Lyubov and V. T. Plakhotnik, "Calculation of the Impurity Distribution in an Epitaxial Film as a Function of Film Thickness Varying with Time," *Kristallografiya*, Vol. 16, No. 5, 1971.

time and the conditions of film growth. They have shown that the impurity distribution, for all practical purposes, is homogeneous.

IV. STRUCTURE AND MORPHOLOGY

Pocza[1] presented an overview of investigations (up to 1967) of thin-film structure and argued that direct observation of thin-film formation yields the most reliable information on film structure. Direct observation of the morphology of the structure produces the most accurate data obtainable as to the form of the grains, their distribution, and their dislocation structure in the low-thickness range of 1000 Å. Usually, the thin-film structure can be described by some characteristic structural properties. To follow structural changes during growth, the film deposition should be conducted under an electron microscope or electron diffractograph.

Gasanov and Stafeev[2] derived a general formula for the surface capacitance of a semiconductor thin film as a function of its thickness and other surface parameters. Basically, they generalized the low-frequency surface-capacitance approximation for semiconductors of semi-infinite geometry to include semiconductors of finite thickness. According to their formula, surface capacitance decreases as semiconductor thickness diminishes.

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[1] J. F. Pocza, "Forming Processes of Directly Observed Vacuum-Deposited Thin Films," *Proceedings of the Second Colloquium on Thin Films*, Akademiai Kiado, Budapest, 1968.

[2] L. S. Gasanov and V. I. Stafeev, "Surface Capacitance of Semiconductor Thin Films," *Fizika i tekhnika poluprovodnikov*, Vol. 2, No. 3, 1968.

ELEMENTAL SEMICONDUCTORS

Sorokin and others[3] are investigating the structure of silicon surface layers after oxygen diffusion. They have found that oxygen diffusion does not lead to the formation of new crystal dislocations, as would be expected in the region of the maximum gradient of impurity diffusion.

Pavlov and Pashkov[4] examined the equilibrium dislocation structure of B and P diffusion layers (arbitrarily oriented) in Si. They discovered that equilibrium dislocation arrays are formed in three configurations of edge and 73° dislocations. Structural peculiarities in (011) dislocation arrays during phosphorous doping were used to compute the energy of nuclei in Si edge dislocations. Using this approach, the researchers obtained a value of 3.8 ev for the energy; on the basis of conventional dislocation-theory formulas, they computed a value of 3.4 αev, where $\alpha = 1-2$.

Bendik and others[5] are working on the effect of rapidly diffusing impurities on dislocation etching in silicon. They cite experimental results on the etching of dislocation pits in silicon after abrupt annealing (in glycol) at high temperatures ($<$ 1200° C) in the presence of the transition elements Cr, Mn, Fe, Ni, and Cu.

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[3] L. M. Sorokin, T. P. Timasheva, S. V. Rychkova, and O. N. Efimov, "Structure of the Silicon Surface Layer after Oxygen Diffusion," *Fizika tverdogo tela*, Vol. 13, No. 1, 1971.

[4] P. V. Pavlov and V. I. Pashkov, "Equilibrium Dislocation Structure of B and P Arbitrarily Oriented Diffusion Layers in Si," *Fizika tverdogo tela*, Vol. 12, No. 11, 1970.

[5] N. T. Bendik, V. S. Garnyk, and L. S. Milevskiy, "Effect of Rapidly Diffusing Impurities on Dislocation Etching in Silicon," *Fizika tverdogo tela*, Vol. 13, No. 6, 1971.

Akimchenko and Lyutovich[6] have done work on determining the width of the forbidden band in epitaxial layers of Si-Ge alloys in MOS structures. They have experimented with alloys containing 0 to 18 percent Ge and found widths of 1.07 to 0.98 ev, respectively.

Amrinov and others[7] have developed a method for calculating bulk life time in epitaxial films. The technique makes use of the process involved in the restoration of equilibrium in the concentration of majority carriers in isolated crystals in a state of free-carrier depletion.

Pavars and others[8] are investigating the structure of amorphous films of Si (50-70 Å) and Cr (120-150 Å) via analysis of radial distribution functions. They obtained the following values for coordination shell radii (r_i Å) and coordination numbers (z_i):

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[6] I. P. Akimchenko and K. L. Lyutovich, "Determining the Forbidden Band in an Epitaxial Layer of Si-Ge Alloy in an MOS Structure," *Fizika i tekhnika poluprovodnikov*, Vol. 5, No. 5, 1971.

[7] N. M. Amrinov, G. M. Guro, N. F. Kovtonyuk, and E. N. Lebedev, "Calculation of Bulk Life Time in Epitaxial Films Via the Method of Isolated Crystals," *Fizika i tekhnika polupiovodnikov*, Vol. 4, No. 9, 1970.

[8] I. A. Pavars, B. A. Baum, P. V. Geld, and G. S. Yurev, "Structure of Amorphous Films of Silicon and Chromium," *Kristallografiya*, Vol. 16, No. 3, 1971.

Table 1

STRUCTURE OF AMORPHOUS Cr AND Si FILMS

Material	Structure	r_1	z_1	r_2	z_2	r_3	z_3	r_4	z_4
Cr	Amorphous films	2.56	10.6	3.65	11.4	4.52	16.8	5.30	24.2
Cr	bcc	2.48	8	2.87	6	4.07	12	4.97	8
Cr	fcc	2.56	12	3.62	6	4.43	24	5.12	12
Si	Amorphous films	2.66	8.1	3.02 3.50	0.7 6.0	4.10	9.9	5.72 5.22	13
Si	Simple cubic	2.55	6	3.60	12	4.42	8	5.10	6
Si	bcc	2.58	8	2.99	6	4.22	12	5.16	8
Si	fcc	2.66	12	3.76	6	4.60	24	5.32	12
Si	Diamond	2.35	4	3.84	12	4.50	12	5.43	6

In this fashion, they concluded that the distribution of atoms in thin (up to 150 Å) amorphous films of Si and Cr is not identical with that corresponding to the films' stable crystalline forms.

Zavaritskaya has reported three interesting studies on Ge films,[9] which basically, involve the investigation of impact ionization in very thin (2-3μ) Ge films at low temperatures (< 4.2° K). She found that breakdown -- manifested by a sudden rise in current (3-4 orders of magnitude) -- occurred in the films at a voltage equal to the ionization potential of the uncompensated impurity atoms. Since the field intensity in such films does not exceed several tens of volts per cm, the sudden rise in current could not be explained by the tunneling effect. The explanation, according to the author, lies in the impact ionization of group III and V impurities.

[9] E. I. Zavaritskaya, "Electrical Discharge in Ge Thin Films at Low Temperatures"; "Impact Ionization of Impurities in Germanium at Low Temperatures"; and "Electrical Conductivity of Zinc-Doped Germanium," *Trudy fizicheskogo instituta im. P. N. Lebedeva*, Vol. 37, 1967.

Gippius' work[10] on the recombination radiation of germanium crystals with dislocations has yielded new data on the mechanism of radiative recombination at dislocations and on the energy structure of "radiators" associated with dislocations. The introduction of the concept of intracenter transitions taking place at "radiators" which are various imperfections in the dislocation structure made it possible to explain several phenomena observed in the investigation of the recombination radiation of crystals with dislocations -- in particular, the dependence of the emission band intensity on the injection current and dislocation density. Analysis of the shape of the emission band yielded some information on the role of phonons in the radiative recombination at dislocations. The problem of the mechanism of radiative recombination was not regarded as fully solved. Although the concept of intracenter transitions was found to be very useful, the energy of excited states and the lifetime of a hole in an excited state remain unknown. To determine the values of these parameters, one would need to study the kinetics of recombination radiation. Moreover, the measurements should be carried out at lower temperatures.

Luby and others[11] have reported on the dependence of crystal structure and charge-carrier mobility in thin Ge films on condensed atom energy. Films were prepared via cathode sputtering at a rate of 0.3-0.4 μ/hr on Ge and NaCℓ substrates at temperatures of 225-450° C and pressures of $\sim 10^{-3}$ mm Hg.

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[10] A. A. Gippius, "Recombination Radiation of Germanium Crystals with Dislocations," ibid.

[11] Sh. Luby, Ya. Chervenyak, and Ya. Shilder, "Dependence of Crystal Structure and Charge Carrier Mobility in Ge Thin Films on Condensed Atom Energy," *Fizika tverdogo tela*, Vol. 12, No. 5, 1970.

Dubinskiy's and Lebedev's work[12] involved structural analysis of angular distributions arising in the sputtering of various single-crystals (Ge, InSb, Re, and Cu) via Ar^{40} ion bombardment at 70 kev.

A^2B^6 COMPOUNDS

Shalimova and Dmitriev[13] are investigating the texture of obliquely evaporated CdS films.

Vovsi and Strakhov[14] are studying the effects of gas adsorption (particularly O_2) on internal stresses in CdTe films obtained through vacuum deposition (10^{-8} torr vacuum) on cold mica and quartz substrates. They have found the following correlation between O_2 pressure (P), internal stress (S), and resistivity (R):

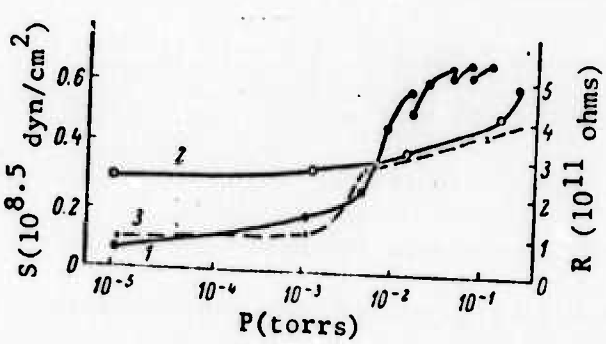

Fig 2 -- Variation of internal stress and resistivity with O_2 pressure. 1 - In the presence of O_2; 2 - without O_2 and no annealing; 3 - with variable resistivity and O_2.

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[12] V. E. Dubinskiy and S. Ya. Lebedev, "Fine Structure in Angular Distributions During the Sputtering of Single-Crystals," *Fizika tverdogo tela*, Vol. 12, No. 8, 1970.

[13] K. V. Shalimova and V. A. Dmitriev, "Texture of Obliquely Evaporated CdS Films," *Kristallografiya*, Vol. 17, No. 1, 1972.

[14] A. I. Vovsi and L. P. Strakhov, "Effect of Oxygen on Internal Stresses in Cadmium Telluride Films Obtained through Vapor Deposition," *Fizika i tekhnika poluprovodnikov*, Vol. 12, No. 11, 1970.

Internal stress was computed from the Stoney formula without taking Poisson's ratio into consideration.

Shaldervan and Nakhodkin[15] are studying the structure and morphology of selected polycrystalline thin films (Aℓ, Au, Ag, Cr, Bi, Te, and CdTe) and amorphous Ge films of 100-1000 Å in thickness. The films were prepared by vacuum deposition (10^{-6} mm Hg) at a rate of 50-1000 Å/min. The direction of vapor inflow (relative to the substrate) was varied from 0° to 80°. Analysis showed that obliquely deposited films of CdTe and other materials consisted of acicular crystals whose axes were inclined in the direction of molecular-beam incidence.

A^3B^5 COMPOUNDS

Frantsevich and others[16] have examined the energy spectrum and structure of BN in all four of its crystalline forms -- i.e., hexagonal graphite (1), rhombohedral graphite (2), cubic sphalerite (3), and hexagonal wurtzite (4). They found that in BN(4) the regular tetrahedral configuration of B and N atoms is disturbed and that the bond length in the direction of the B-B or N-N axis is longer than in other directions, which brings BN(4) closer to BN(1), where bond anisotropy is extremely great. And, irrespective of differences in spectra and bond length between BN(3) and BN(4), the latter (according to its energy and crystal structure) is considerably closer to BN(3) than to BN(1).

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[15] A. I. Shaldervan and N. G. Nakhodkin, "Profiles of Selected Thin Condensed Film," *Fizika tverdogo tela*, Vol. 12, No. 7, 1970.

[16] I. N. Frantsevich, E. A. Zhurakovskiy, A. V. Kurdyumov, and N. N. Vasilenko, "Energy Spectrum and Thin Wurtzite Structure of Boron Nitride," *Doklady AN SSSR*, Vol. 203, No. 1, 1972.

Bolkhovityanov and others[17] recently completed a study on the influence of structure on certain properties of GaAs epitaxial films. Among other findings, they registered anomalously high values for transverse magnetoresistance and its anisotropy relative to the orientation of the magnetic field -- parallel and perpendicular to the film surface. Also, they found that the thickness of the film and the size of the magnetic field play a critical role in determining film properties.

Komilov and others[18] are working on the compensation of high-resistance epitaxial GaAs films using impurities with deep energy levels. The authors obtained high-resistivity (10^2 - 10^5 ohm cm rather than the typical 0.5 ohm cm) n-type GaAs films via synthesis from Ga and $AsCl_3$ on semiinsulated chromium-doped substrates. They found that chromium atoms and complex lattice defects play a role in the compensation of the said films.

Lisenker and others[19] recently examined the influence of substrate orientation on the doping level and the distribution of impurities in GaAs epitaxial films. The films were obtained via vapor transport

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[17] Yu. B. Bolkhovityanov, A. F. Kravchenko, B. V. Morozov, and E. M. Skok, "Kinetic Effects in Epitaxial Semiconductor Films," *Fizika i tekhnika poluprovodnikov*, Vol. 5, No. 6, 1971.

[18] B. V. Komilov, V. A. Vilkotskiy, G. V. Aleksandrova, G. N. Tereshko, and T. P. Tsarevskaya, "Compensation of High-Resistance Epitaxial Films of Gallium Arsenide Using Impurities with Deep Energy Levels," *Fizika i tekhnika poluprovodnikov*, Vol. 5, No. 1, 1971.

[19] B. S. Lisenker, P. E. Maronchuk, Yu. E. Maronchuk, and A. P. Sherstyakov, "Influence of the Plane of Orientation on the Doping Level and the Distribution of Impurities in GaAs Epitaxial Films," *Neorganicheskie materialy*, Vol. 8, No. 4, 1972.

techniques ($Ga-AsCl_3-H_2$) on substrates of semiinsulated GaAs with a resistivity of $\sim 10^6$ ohm cm oriented in different fashions -- i.e., (111)A, (111)B, (110), (100), and inclined from (100) toward (111)B at angles of 5, 9, 12, 20, 35, and 45°.

$A^3B^5C^6$ COMPOUNDS

Palatnik and others[20] investigated the structure and properties of $TlBiS_2$ semiconductor films. The films were prepared by means of vacuum evaporation in a $\sim 5 \times 10^{-5}$ torr vacuum on glass and single-crystal NaCl substrates with (001) orientation at a rate of 1 Å/sec. The substrate temperature was 20° C to ensure 100 percent condensation of the evaporated material. The films were subsequently annealed in a vacuum at temperatures of 100-500° C. It was found that the $TlBiS_2$ compound was isostructurally similar to a compound studied earlier -- $TlBiSe_2$ -- and in thin-film form was an isoelectronic analog of PbS.

A^4B^6 COMPOUNDS

Kosevich and others[21] have done considerable work on the structure of epitaxial lead chalcogenide films on mica substrates. Using electron microscopy, they studied film orientation, growth, annealing, and structural defects in epitaxial PbTe and PbSe films. They found that at substrate temperatures of 150-400° C PbSe films develop crystals oriented in two fashions: (111) [112] and (001) [110] || (001) [010]. In PbTe films, (001) [110] orientation was observed only when temperatures exceeded 280° C. Samples with (111) orientation obtained fine

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[20] L. S. Palatnik, L. P. Zozulya, and L. G. Voinova, "On the Structure and Selected Properties of $TlBiS_2$ Films," *Kristallografiya*, Vol. 16, No. 5, 1971.

[21] V. M. Kosevich, L. S. Palatnik, L. P. Zozulya, L. F. Zozulya, and V. K. Sorokin, "Structure of Epitaxial Lead Chalcogenide Films on Mica," *Fizika tverdogo tela*, Vol. 12, No. 5, 1970.

faceting right from the earliest stages and grew mainly in height. Samples with (001) orientation were flat and thin, and in the early growth stages were characterized by rough contours and a large number of internal cavities. The basic structural defects observed in the PbTe and PbSe films were two-dimensional twinning $\{11\bar{2}\}$ boundaries perpendicular to the plane of the film. During the recrystallization process, these boundaries were transformed into obliquely arranged, distorted boundaries of cylindrical form.

Kosevich also is coauthor of a recent study[22] on the boundary structure in epitaxial SnSe films. The films were obtained by vacuum evaporation at 5 x 10^{-5} torr pressure and substrate temperatures of 250-350° C on a (001) KCℓ crystal face. Prepared in this manner, the films formed flat crystal-conjugate boundaries. Using Moire's electron microscopy technique, researchers found that the majority of the boundaries were of twinned nature. Boundary deviations from strictly twinned orientation result in the appearance of dislocations in their structure. The observed boundaries were characteristic of epitaxial films, whose growth process is of the "vapor → crystal" type without coalescence.

Zakharov and Zaliva[23] are investigating the transition of thin (10^{-5} cm) GeTe and GeSe films from an amorphous state into polycrystalline form. The films were prepared by thermal deposition in a vacuum of 10^{-5} mm Hg on unheated glass substrates. The authors derived the

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[22] V. M. Kosevich, L. S. Palatnik, and S. N. Grigorov, "Investigation of the Boundary Structure in SnSe Films Using the Rotational Moire Method," *Kristallografiya*, Vol. 17, No. 2, 1972.

[23] V. P. Zakharov and V. I. Zaliva, "Conversion of GeTe and GeSe Thin Films from an Amorphous State into Polycrystalline Form," *Kristallografiya*, Vol. 17, No. 1, 1972.

following graph for the distribution of atoms in the amorphous forms of these materials:

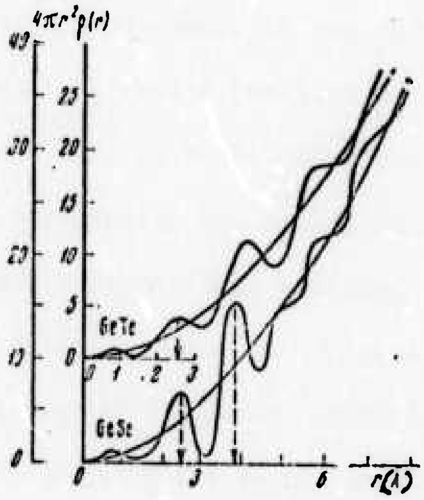

Fig. 3 -- Distribution of atoms in amorphous GeTe and GeSe films.

They also found that film recrystallization can be stimulated via rapid heating, using intense light pulses. Because there is a specific temperature range in which these materials preserve a stable amorphous state, the recrystallization process always begins at a specific temperature. During GeTe recrystallization, the radius of the first coordination shell changes from 2.6 to 3.01 Å; for GeSe the change is not as great (2.5 to 2.6 Å). In both films, the conductivity irreversibly increases as a result of recrystallization (two- to threefold increases for GeSe and four orders of magnitude in the case of GeTe). The authors conclude that these changes in electric properties correspond to changes in structure, and that the complex nature of the structural changes is further underscored by the observation of a significant reversible increase in GeSe conductivity during the early stages of recrystallization.

A^5B^6 COMPOUNDS

Zavyalova and Imamov[24] have developed a structural model of a $Bi_2O_{2.5}$ thin film. In their model, the O atoms are located in tetrahedra of Bi atoms, while the Bi atoms are not arranged in distorted octahedral form but in trigonal prisms of O atoms.

Kremnev and others[25] are using electron diffraction and optical microscopy to study the distribution and orientation of components in solid-solution films of antimony and bismuth tellurides. The $(Bi, Sb)_2 Te_3$ films were obtained by vacuum deposition at 10^{-5} torr pressure on muscovite substrates, using the following reactions:

Sb_2Te_3 (solid) $\Leftrightarrow$ 1/2 Sb_4 (gas) + 3/2 Te_2 (gas) (697-819° K)

Bi_2Te_3 (solid) $\Leftrightarrow$ 2 BiTe (gas) + 1/2 Te_2 (gas) (718-807° K).

They found that dissociation of the initial compounds during vaporization leads to a significant inhomogeneity in the films' composition. Also, substrate temperature has considerable effect on the distribution and orientation of thin-film components.

POLYMER COMPOUNDS

Merkulov and others[26] have studied hole mobility in polydiphenylacetylene films and its high-temperature sublimation. The authors

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[24] A. A. Zavyalova and R. M. Imamov, "On the Structure of Thin Layers of β-$Bi_2O_{2.5}$," *Kristallografiya*, Vol. 16, No. 3, 1971.

[25] V. A. Kremnev, P. A. Leontev, and A. I. Platov, "Distribution and Orientation of Varied Phases in Solid Solution Films of Antimony and Bismuth Tellurides," ibid.

[26] E. I. Merkulov, A. N. Vannikov, and I. D. Mikhaylov, "Hole Mobility in Polydiphenylacetylene Films," *Fizika tverdogo tela*, Vol. 13, No. 9, 1971.

argue that charge-carrier mobility in this polymer (2×10^{-4} cm^2/volt sec) is low because of the presence of a large number of small traps. Carrier mobility in sublimated polydiphenyacetylene -- in which traps are present at a significantly reduced level -- is considerably greater (0.3 cm^2/volt sec).

Galperin and Mindrul[27] reported on the structure of thin oriented films of the copolymer of vinylidenfluoride with tetrafluoroethylene. They studied crystalline and macromolecular structural changes during deformation and subsequent annealing of this copolymer, using electron diffraction and electron microscopy techniques. They found that the annealing of oriented films of this copolymer results in the formation of large, well-defined lattice constants.

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[27] E. L. Galperin and V. F. Mindrul, "Structure of Thin Oriented Films of the Copolymer of Vinylidenfluoride with Tetrafluoroethylene," *Kristallografiya*, Vol. 16, No. 5, 1971.

V. ELECTRICAL AND GALVANOMAGNETIC PROPERTIES

Kravchenko and others[1] have computed the magnetoresistance and Hall coefficient in thin semiconductor films with inhomogeneous distributions of charge carriers (in terms of both concentrations and mobility) along its vertical dimension (thickness). They were able to induce anisotropy in the magnetoresistance by rotating the magnetic field in a plane perpendicular to the current in the thin film. According to the authors, their results can be used to describe galvanomagnetic effects in epitaxial semiconductor films exhibiting transition layers characterized by higher conductivity at the film-substrate interface, as well as thin films with surface concentrations of carriers. The calculations were experimentally verified using epitaxial films of GaAs containing inhomogeneous impurity distributions.

Rusanov,[2] in a recently published paper on the thermodynamics of thin films and electrocapillary phenomena, derived the basic equations governing the thermodynamics of electrocapillary phenomena in thin films.

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[1] A. F. Kravchenko, B. V. Morozov, and E. M. Skok, "Magnetoresistance Anisotropy and Hall Effect in Thin Semiconductor Layers," *Fizika i tekhnika poluprovodnikov*, Vol. 6, No. 2, 1972.

[2] A. I. Rusanov, "On the Thermodynamics of Thin Films and Electrocapillary Phenomena," *Doklady AN SSSR*, Vol. 203, No. 2, 1972.

ELEMENTAL SEMICONDUCTORS

Avakyants and others[3] have studied current variations in silicon compensated by cadmium (10^{-2} % Zn). When high-intensity electrical pulses were acting on the n-Si film at 90° and at a temperature of 77° K, acoustic oscillations were generated which were in phase with the incident-pulse frequency.

Klimovskaya and others[4] have investigated the transverse magnetoresistance anisotropy of thin n-Si films. The n-Si films (.004-.07 cm-thick) were exposed to a wide range of temperatures (20-160° K). Experimental results were subsequently used to derive the relation of magnetoresistance-anisotropy dimensions to the depth and intensity of the magnetic field. The authors concluded that the observed effect was induced by the separation (in the magnetic field) of charge carriers according to energy.

A^2B^5 COMPOUNDS

Bokiy and others[5] have studied the preparation and electrical properties of selected A^2B^5 semiconductor films -- mainly CdSb and Cd_3As_2. They claim to have devised a new way of obtaining A^2B^5 films which, basically, consists of crystallizing a layer of melt compressed between two substrates. The parameters of such films are

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[3] G. M. Avakyants, A. A. Stepanov, and R. S. Barsegyan, "Current ...ns in Silicon Compensated by Cadmium (10^{-2} % Zn)," *Fizika i ...ovodnikc* Vol. 6, No. 3, 1972.

...sk... V. Snitko, and S. I. Kirillova, "Transverse Magneto... Thin Films of Electronic Silicon," *Fizika i ...ov*, Vol. 5, No. 7, 1971.

[5] G. B. ...enko, G. I. Goncharenko, A. D. Goncharov, P. Rudolf, I. ... V. Sandulova, and L. D. Khutoryanskiy, "Preparation and Elec... ...perties of Selected A^2B^5 Semiconductor Thin Films," *Doklady A...* Vol. 200, No. 1, 1971.

said to be as good as those of single-crystals and, in some instances, better than those of vacuum-deposited films. The result of their study is in the form of three graphs (Figs. 4-6):

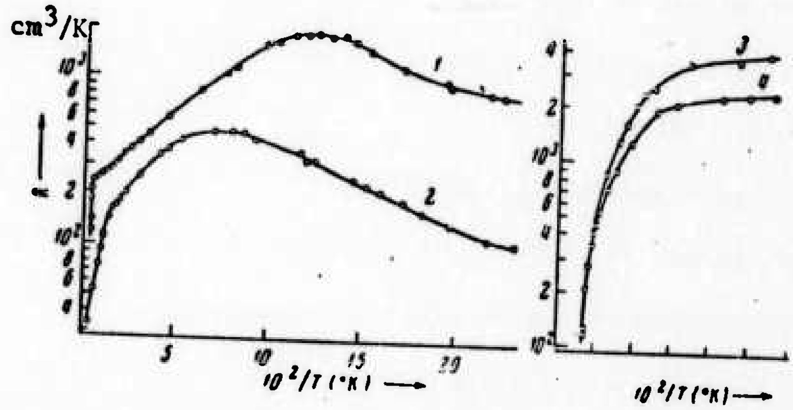

Fig. 4 -- Variation of the Hall constant R(T) with temperature (T) in CdSb
1 - Film thickness of 25μ; 2 - film thickness of 150μ; 3 - compensated with Te; 4 - compensated with Se.

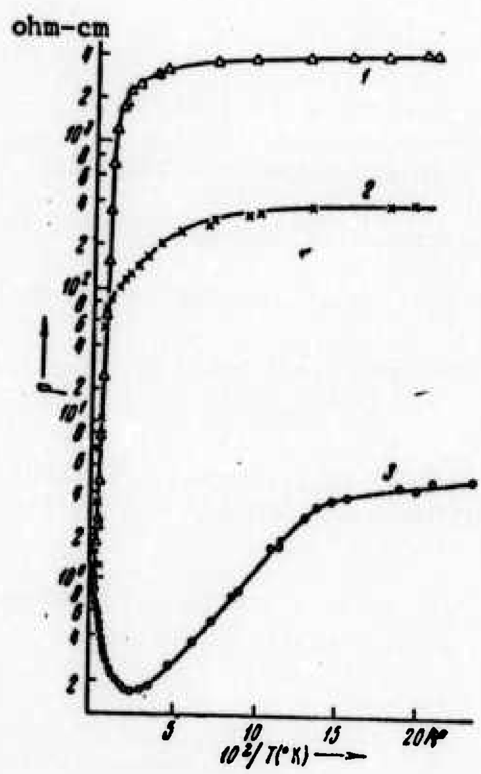

Fig. 5 -- Variation of resistivity ρ(T) with temperature in p-CdSb.

1 - Compensated with Te and Se;
2 - compensated with Aℓ; 3 - undoped.

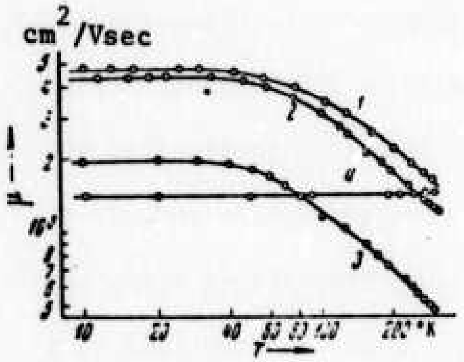

Fig. 6 -- Plot of mobility vs temperature.

1, *2*, 3, - Films 20-100μ - thick; 4 - film obtained via vacuum deposition.

A^2B^6 COMPOUNDS

Karpovich and others[6] investigated the field effect in CdSe films (coated with an SiO film) during large fluctuations in the surface potential. They derived the relation of surface conductivity, effective mobility, and field-effect kinetics to the dark surface potential.

Karpovich[7] also published a paper on the residual conductivity in CdSe films. He showed that the magnitude of the residual conductivity is a function of field intensity and is independent of the level of applied photostimulation (provided that during irradiation a steady state is achieved). Also, a longitudinal electric field serves to quench residual conductivity.

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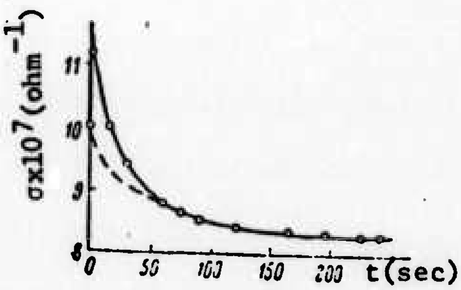
[6] I. A. Karpovich, S. V. Tikhov, and A. N. Kalinin, "Field Effect in CdSe Films during Large Fluctuations in the Surface Potential: Dark Characteristics," *Fizika i tekhnika poluprovodnikov*, Vol. 4, No. 9, 1970.

[7] I. A. Karpovich, B. N. Zvonkov, and M. A. Lizakhanov, "Residual Conductivity in CdSe Films," *Fizika tverdogo tela*, Vol. 12, No. 8, 1970.

A^4B^6 COMPOUNDS

Ilin[8] has studied the effect of hydrogen on the conductivity of lead sulphide polycrystalline films. He found that hydrogen molecules with extremely high adiabatic ionization potential incident on the surface of a semiconductor can serve as electron donors and, in the particular case of PbS, can affect certain properties -- e.g., photosensitivity and electrical conductivity. He derived the following graph showing PbS conductivity as a function of the time it resides in a hydrogen atmosphere:

Fig. 7 - PbS film conductivity



A^3B^5 COMPOUNDS

Emelyanenko and others[9] investigated the magnetoresistance in n-GaAs epitaxial films and found it to be a function of temperature,

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[8] V. I. Ilin, "Effect of Hydrogen on the Conductivity of Lead Sulphide Polycrystalline Films," *Fizika i tekhnika poluprovodnikov*, Vol. 5, No. 4, 1971.

[9] O. V. Emelyanenko, D. N. Nasledov, D. D. Nedeoglo, and I. N. Timchenko, "Magnetoresistance in n-GaAs Epitaxial Layers," *Izvestiya AN MoldSSR*, No. 1, 1972.

magnetic field intensity, and film orientation. They developed the following two graphs (Figs. 8 and 9) showing these relationships:

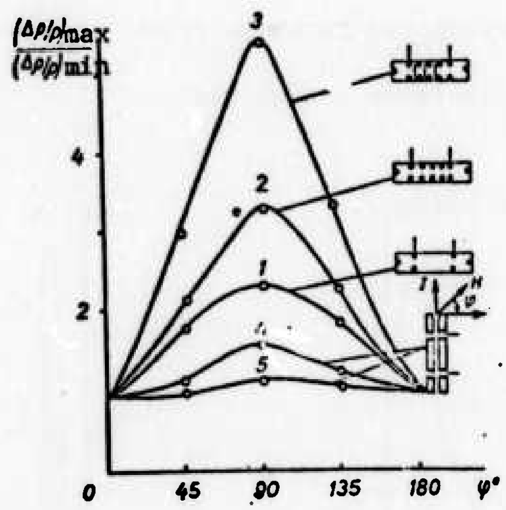

Fig. 8 - Relation of transverse magnetoresistance to the film's angle of rotation in the magnetic field.

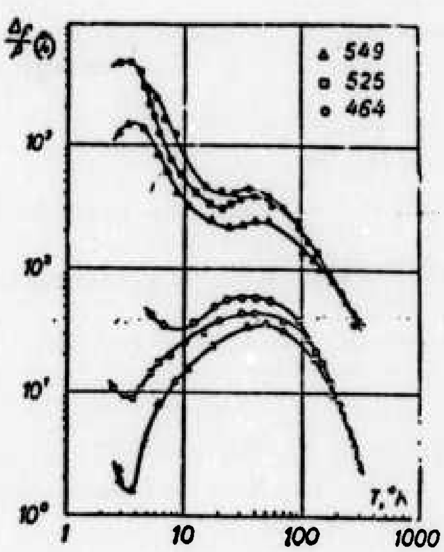

Fig. 9 - Variation of magnetoresistance with temperature.

Zhdan and Messerer[10] studied thermostimulated conductivity in thin films of single-crystal CdS and GaAs (in a vacuum creostate) on the basis of several models (developed by them) of electrically active, thermostimulated desorption in these films. They derived the following graphs for thermostimulated conductivity:

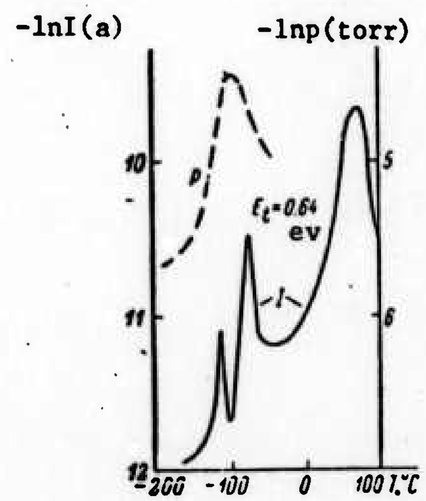

Fig. 10 - CdS (.5μ-thick).
I - Current; T - temperature; p - pressure in creostat; E_t - trap energy level.

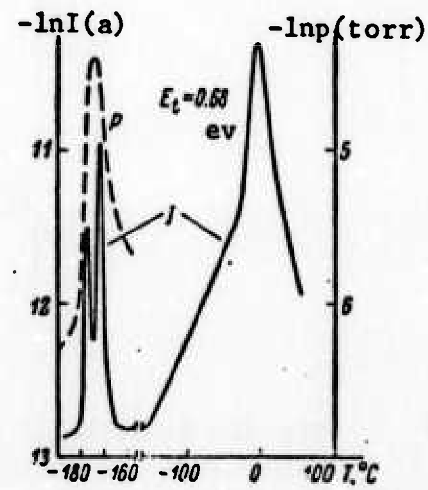

Fig. 11 - GaAs (100μ-thick, Cr-doped).
I - Current; T - temperature; p - pressure in creostat; E_t - trap energy level.

$BaTiO_3$ AND POLYMER COMPOUNDS

Gavrilova and others [11] used the pyroelectric effect in $BaTiO_3$ and triglycinsulfate (TGS) films to study saturation polarization and its dependence on temperature and film thickness. Gavrilova selected these

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[10] A. G. Zhdan and M. A. Messerer, "Electrically-Active Thermo-stimulated Desorption in Thin CdS and GaAs Single-Crystals," *Fizika tverdogo tela*, Vol. 13, No. 1, 1971.

[11] N. D. Gavrilova, Yu. A. Zvirgzd, V. K. Novik and V. G. Poshin, "Pyroelectric Effect in Thin Triglycinsulfate (TGS) and $BaTiO_3$ Films," *Fizika tverdogo tela*, Vol. 13, No. 6, 1971.

well-studied films for her experiments because their characteristics are well known and are easy to obtain in film form. The graphs in Figs. 12 and 13 illustrate the findings of this study.

Petrova and Rozenshteyn[12] studied the field effect and slow states in thin films of several organic semiconductors -- e.g., pentacene, tetrathiotetracene (TTT), and pinacyanol. The observed field effect was used to determine precisely the conductivity of the aforementioned materials. Petrova and Rozenshteyn found that, despite the high resistivity in the transverse field, the films exhibited carrier depletion and concentration phenomena. The photosensitive films exhibited greater sensitivity to the transverse field when irradiated. Further, slow states were found to be characteristic of organic semiconductors. The films were obtained by vacuum deposition (10^{-5} torr pressure) and were .1-.5μ thick. Pentacene exhibited high-ohmic properties and had a conductivity of $\sim 10^{-10}$ amp (hole conductivity). TTT was a low-ohmic material with a conductivity of 10^{-6} -10^{-5} amp; the transverse magnetic field generated variations of up to 50 percent in the conductivity. Pure pinacyanol is an extremely high-ohmic material but, when doped with tetracyanquinodimethane, has a conductivity of $\sim 10^{-6}$ amp, which can vary up to 250 percent depending on the transverse field.

Blagodarov and others[13] investigated the nonequilibrium AC conductivity of phtalocyanin films. The films were prepared via sputtering

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[12] M. L. Petrova and L. D. Rozenshteyn, "Field Effects and Slow States in Thin Films of Organic Semiconductors," *Fizika tverdogo tela*, Vol. 13, No. 8, 1971.

[13] A. N. Blagodarov, E. L. Lutsenko, and L. D. Rozenshteyn, "Nonequilibrium AC Conductivity of Phtalocyanin Layers," *Fizika tverdogo tela*, Vol. 12, No. 5, 1970.

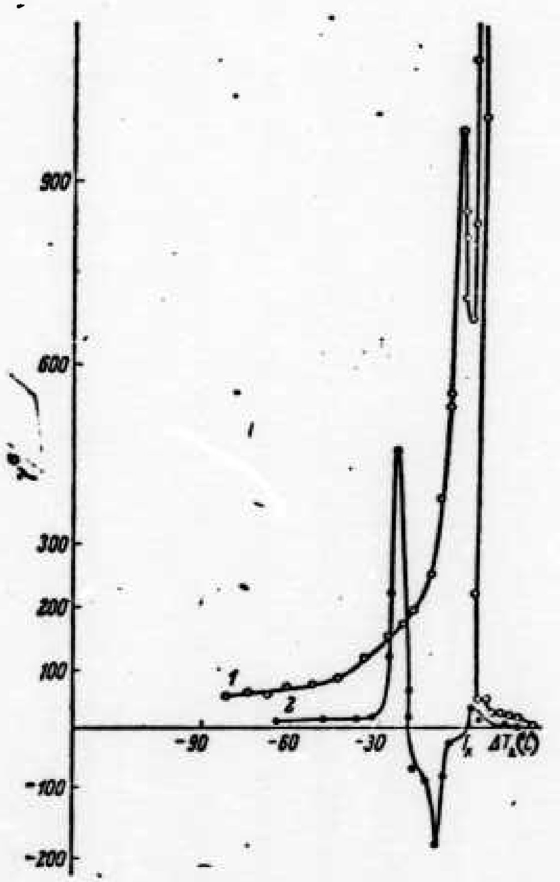

Fig. 12 - Variation of the pyroelectric coefficient (γ^{σ}) for $BaTiO_3$ with temperature.

1 - 15μ-thick film; 2 - 350μ-thick film.

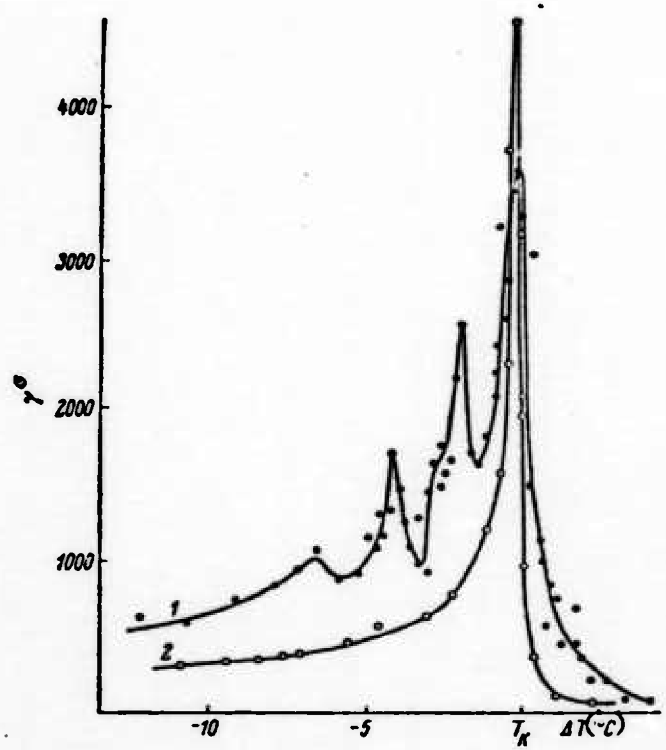

Fig. 13 - Variation of the TGS pyroelectric coefficient (γ^{σ}) with temperature.

1 - 1000μ-thick TGS film; 2 - 50μ-thick TGS film.

in a 10^{-4} torr vacuum at 140° C (film thickness was .5-1.0μ). A photodielectric effect (associated with changes in polarization) was observed when the film was exposed to high temperatures. Observed variations in conductivity were attributed to traps -- necessary links in the charge-carrier transport mechanism.

Ganushchak and others[14] are studying the electrical conductivity of diphenylpolyene (DFP) films -- e.g., stilbene, diphenylbutadiene (DFB), diphenylhexatrien (DFHT), and diphenyloctatetraene (DFOT). The output of this study was mainly in the form of a table and two graphs showing electrical conductivity and its dependence on temperature:

Table 2

ELECTROCONDUCTIVITY OF DFP FILMS

Material	σ (ohm^{-1})	$\Delta E \pm 0.05$ (ev)	σ_0 (ohm^{-1}cm^{-1})
Stilbene	4.10^{-16}	0.87	$4.25.10^{-1}$
DFB	$2.1.10^{-15}$	0.76	$2.48.10^{-2}$
DFHT	$5.5.10^{-15}$	0.72	$1.31.10^{-2}$
DFOT	2.10^{-14}	0.65	$3.6\ .10^{-3}$

[14] N. I. Ganushchak, N. I. Gritsenko, and M. V. Kurik, "Electroconductivity of Diphenylpolyene Films," *Fizika tverdogo tela*, Vol. 14, No. 4, 1972.

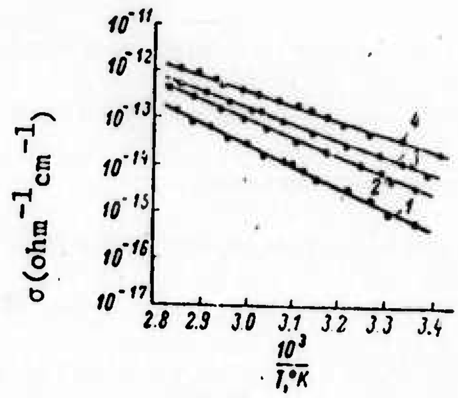

Fig. 14 - Film conductivity as a function of temperature.

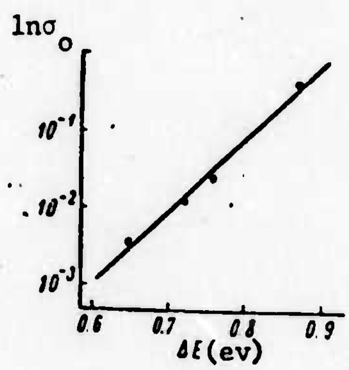

Fig. 15 - Log σ_0 as a function of ΔE for DFP films.

VI. ACOUSTIC PROPERTIES

Margulis[1] has studied oscillations of electrical conductivity in films in a transverse quantizing magnetic field due to electron scattering by optical phonons. He has shown that two oscillation periods (associated with spectral discreteness) appear in the case of a degenerate electronic gas. Further, these oscillations can also arise in the nondegenerate case.

Baskin and Entin[2] have investigated the effect of a film's surface on electron-phonon interaction, particularly electron-scattering by Rayleigh waves. In the isotropic continuous-medium approximation, Baskin and Entin determined relaxation times during electron-scattering by surface irregularities generated by transverse acoustic phonons and scattering by flexural waves. They found that energy transfer due to various processes is small and cannot lead to a cooling of carriers at the surface due to radiation of acoustical or optical phonons.

Garevskiy and Orlova[3] have studied oscillations in thin-film conductivity in a quantizing magnetic field due to electron-scattering by optical phonons. As reported by them, quantizing electron movement in films lead to a division of the current oscillation maximum

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[1] V. A. Margulis, "Conductivity Oscillations in Films," *Fizika tverdogo tela*, Vol. 13, No. 4, 1971.

[2] E. M. Baskin and M. V. Entin, "Effect of Film Surface on Electron-Phonon Interaction," *Fizika tverdogo tela*, Vol. 13, No. 3, 1971.

[3] A. S. Garevskiy and N. E. Orlova, "Oscillations in Thin-Film Conductivity in a Quantizing Magnetic Field due to Electron Scattering by Optical Phonons," *Fizika i tekhnika poluprovodnikov*, Vol. 6, No. 1, 1972.

(characteristic of large samples) into two close maxima. Transitions between various film-energy levels complicate the relation of current to the magnetic field potential.

VII. OPTICAL PROPERTIES

Bass and Matulis[1] investigated an analog of the cyclotron-phonon resonance in semiconductor films. They showed that the absorption coefficient of an electromagnetic wave in a thin film undergoes jump wise changes in a field whose frequency (ω) is equal to $\omega_{ss'} \pm \omega_0$, where $\omega_{ss'}$ corresponds to the distance between the s and s' electron energy levels and ω_0 represents the optical-phonon frequency. Quantization of the electron energy spectrum was found to be dependent upon the finite dimensions of the thin film.

ELEMENTAL SEMICONDUCTORS

Kozyrev and Osipov[2] studied the spectral distribution of the nonstationary photomagnetic effect in thin (4-45μ) optically polished single-crystal n-Ge films ($\rho \approx 20$ ohm cm and $n = 2 \times 10^{14}$ cm^{-3}) and p-Ge films ($\rho \approx 32$ ohm cm and $n = 5 \times 10^{12}$ cm^{-3}) in the range $\lambda = 0.5$-2.0 μ, at 395 Hz. Their results were illustrated by a graph showing photomagnetic sensitivity (ε'_λ) of Ge films with a [11$\bar{2}$] orientation, irradiated from the surface exhibiting the more rapid recombination as a function of irradiation wavelength.

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[1] F. G. Bass and A. Yu. Matulis, "Dimensional-Phonon Jumps of Light Absorption in Semiconductor Films," *Fizika tverdogo tela,* Vol. 12, No. 7, 1970.

[2] B. P. Kozyrev and Yu. V. Osipov, "Spectral Distribution of the Photomagnetic Effect in Ge Thin Films," *Fizika poluprovodnikov,* No. 1, 1968.

Matveeva[3] observed deformational splitting of the impurity absorption band in heteroepitaxial p-germanium. While investigating the optical properties of these Ge films, she uncovered a double spectral line, whose position and intensity was a function of the film's crystalline structure. The following graph shows variations in the absorption coefficient in Ge films of varied structure (at room temperature):

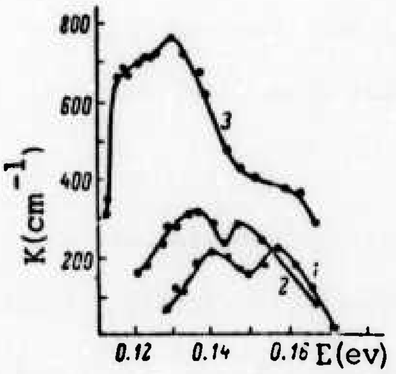

Fig. 16 - Variation of the absorption coefficient in Ge films.

1 - Perfect single-crystal; 2 - mosaic single-crystal; 3 - textured single-crystal.

The author further notes that the study of the deformational splitting of the valence band by means of impurity absorption (associated with deep acceptor levels) opens new approaches to the investigation of semiconductor energy.

A^2B^6 COMPOUNDS

Gorodetskiy and others[4] obtained photosensitive films of CdTe by bombarding Te films with Cd^+ ions. The Te film was $\sim$.1 μ in thickness;

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[3] L. A. Matveeva, "Deformational Splitting of the Impurity Absorption Band in Heteroepitaxial p-Type Germanium Films," *Fizika i tekhnika poluprovodnikov,* Vol. 5, No. 11, 1971.

[4] A. E. Gorodetskiy, G. A. Kachurin, N. B. Pridachin, and L. S. Smirnov, "Obtaining Semiconductor Thin Films via Ion Bombardment," *Fizika poluprovodnikov,* No. 1, 1968.

the Cd^+ ions had energies of 5-50 kev; substrate temperature was 50° C. The films thus prepared had typical CdTe optical properties, as illustrated by the following graph:

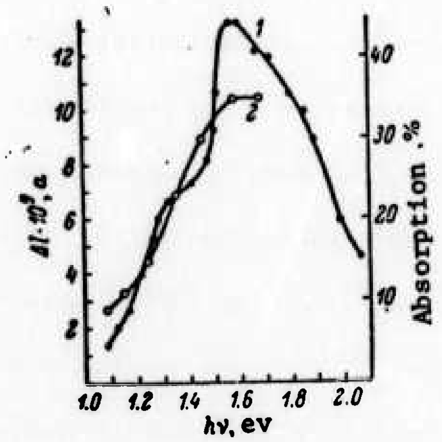

Fig. 17 -- Ohmic properties of CdTe films
1 - Variations in photocurrent; 2 - absorption curve.

Shalimova and others[5] have studied the ohmic properties of polycrystalline CdTe films, particularly the parameters of photosensitive centers. The 5-20 μ-thick films were obtained by vacuum deposition and were doped with iodine to increase their photosensitivity. The films had a dark conductivity of $10^6 - 10^{-8}$ ohm^{-1}. Electron mobility fluctuated from 10 to 100 cm^2 /v sec -- mobility increased as irradiation increased. At temperatures below 200° K, optical and thermal quenching of photoconductivity was observed, as well as superlinearity of lux-ampere characteristics and photocurrent instability with certain irradiation. These phenomena were explained on the basis of the existence

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[5] K. V. Shalimova, E. N. Voronkov, L. N. Muravev, and A. D. Ryazantsev, "Determining the Parameters of Photosensitive Centers in Cadmium Telluride Films," *Fizika i tekhnika poluprovodnikov*, Vol. 6, No. 3, 1972.

of two energy centers (E_v + [0.04 ± 0.05] and E_v + [0.87 ± 0.05]E_v). For the E_v + 0.40E_v center, the photon capture coefficient is $S = 10^{-15} - 10^{-16}$ cm^2, the electron capture coefficient is S_n = (1-5) x 10^{-20}, and the hole capture coefficient is $S_p = 10^{-15} - 10^{-16}$ cm^2.

Karpovich and others[6] are investigating surface impurity photoconductivity (SIP) and induced impurity photoconductivity (IIP) in single-crystal CdSe films, obtained by vacuum evaporation on mica substrates. The films had a dark conductivity of $\sigma_0 \lesssim 10^{-6}$ ohm^{-1} cm^{-1} at 300° K and $\sigma < 10^{-11}$ ohm^{-1} cm^{-1} at 100° K, and exhibited a high level of photosensitivity. The film's surface state was varied by means of controlled deposition of indium with surface concentrations of $N_s \lesssim 10^{15}$ cm^{-2}. The indium deposition increased σ_0 by 5-6 orders of magnitude. The following graph shows the findings of this particular study:

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[6] I. A. Karpovich, M. A. Rizakhanov, and A. N. Kalinin, "Surface Impurity Photoconductivity in CdSe Films," *Fizika i tekhnika poluprovodnikov*, Vol. 4, No. 10, 1970.

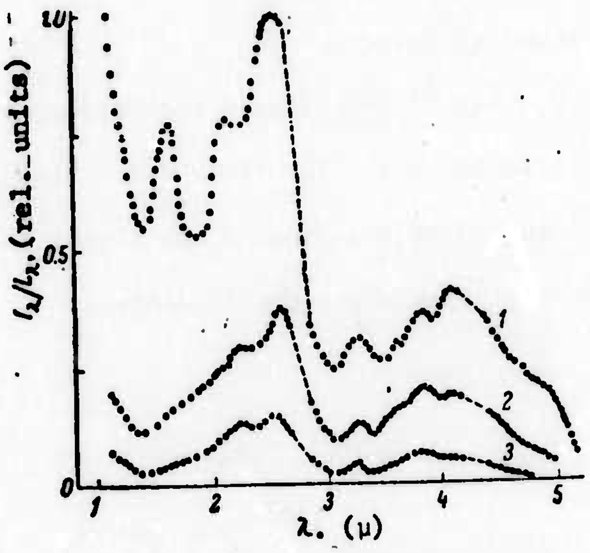

Fig. 18 - Impurity photoconductivity of CdSe films.
1 - IIP; 2 - SIP at $N_s \simeq 8 \times 10^{14}$ cm^{-2};
3 - SIP at $N_s \simeq 2 \times 10^{14}$ cm^{-2}.
Dashed lines represent regions of absorption by atmospheric water vapor and CO_2.

Karpovich and others[7] observed the quenching of residual conductivity by a longitudinal electric field and infrared irradiation. The infrared irradiation quenching spectrum was found to coincide with the spectrum for the infrared-irradiation quenching of photoconductivity.

Kireev and others[8] investigated exciton absorption lines and photosensitivity of epitaxial cadmium selenide films of varied thickness (0.5-3 μ) on sapphire and fluorite substrates. They demonstrated that the position of the exciton lines is a function of film thickness

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[7] I. A. Karpovich, B. N. Zvonkov, and M. A. Rizakhanov, "Residual Conductivity in CdSe Films," *Fizika tverdogo tela,* Vol. 12, No. 8, 1970.

[8] P. S. Kireev, A. G. Kornitskiy, and N. M. Kondaurov, "Exciton States in Epitaxial Layers of CdSe on Sapphire and Fluorite Substrates," *Fizika i tekhnika poluprovodnikov,* Vol. 5, No. 7, 1971.

and the type of substrate used. The spectral lines for photosensitivity and absorption were found to coincide.

Miloslavskiy and others[9] investigated the Faraday effect in thin CdS films near the intrinsic edge. The films were obtained by vacuum evaporation (5×10^{-5} mm Hg) on underheated substrates at a rate of 200 Å/min. The following graph shows the findings.

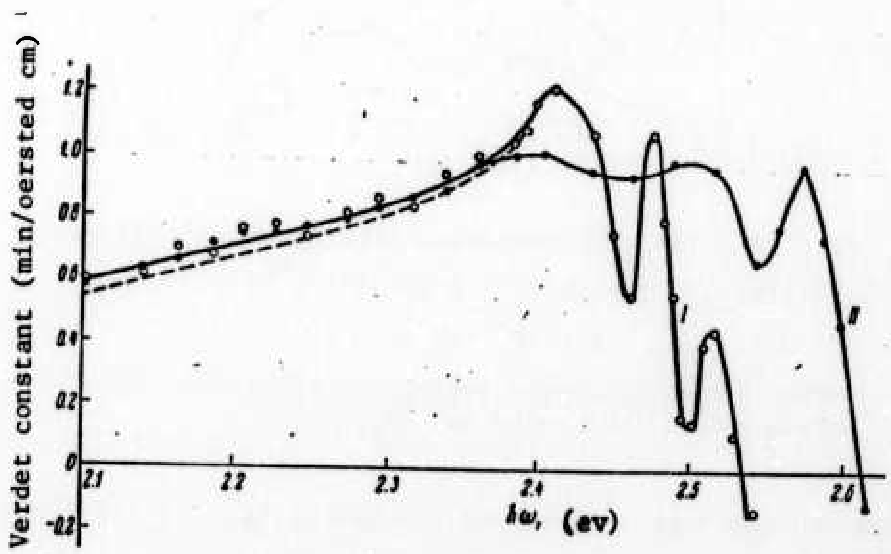

Fig. 19 - Relation of the Verdet constant to energy
(T = 300° K, H = 21 ke).

I - CdS film vacuum annealed at 500° C; II - CdS film prior to annealing. Dashed line indicates findings for single-crystals.

Lazneva and Bykova[10] used the "light-impact" technique to study the photoconductivity of thin (~1 μ) epitaxial cadmium sulphide films. They showed that the observed lux-ampere and relaxation characteristics

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[9] V. K. Miloslavskiy, V. V. Karmazin, and A. A. Shapiro, "Faraday Effect in Thin CdS Films in the Region of the Intrinsic Edge," *Fizika i tekhnika poluprovodnikov*, Vol. 2, No. 4, 1968.

[10] E. F. Lazneva and T. T. Bykova, "Photoconductivity of Cadmium Sulphide Epitaxial Layers," *Fizika i tekhnika poluprovodnikov*, Vol. 6, No. 3, 1972.

of photoconductivity in CdS films purified of oxygen can be interpreted on the basis of a model with two types of recombination centers and levels of film adhesion. Oxygen adsorption on the film surface was observed in two ways via graphs of photoconductivity relaxation. First, in the region of high photoelectron concentration ($> 1.5 \times 10^{15}$ cm^{-3}), the characteristic reduction in the rate of decrease of photoconductivity becomes more pronounced with increases in irradiation intensity. Second, the relaxation curves in the temporal region of > 1 sec clearly revealed an increase in the rate of decrease of photoconductivity, as compared with relaxation curves for films purified of adsorbed oxygen. The authors concluded that these relaxation curves show that oxygen adsorption leads to the appearance of slow surface states which interact with both the valence band and the conduction band.

Karmazin and Miloslavskiy[11] examined the Faraday effect in polycrystalline ZnSe films near the intrinsic edge. Films were obtained by vacuum deposition (10^{-5} torr) on heated (70-350° C) substrates at a rate of 8-11 Å/sec, followed by vacuum annealing.

Dokholyan and others[12] have examined the peculiarities of an electrically induced photoeffect in CdS. Basically, this effect involves the appearance of an impurity photosensitivity as a result of the filling of impurity centers due to the passage of current via monopolar injection through the semiconductor.

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[11] V. V. Karmazin and V. K. Miloslavskiy, "Faraday Effect in Polycrystalline ZnSe Films in the Region of the Intrinsic Edge," *Fizika i tekhnika poluprovodnikov*, Vol. 5, No. 5, 1971.

[12] Zh. G. Dokholyan, Yu. A. Zubyts, L. G. Paritskiy, and A. I. Rozental, "Peculiarities of Electroinduced Photoeffect in CdS," *Fizika i tekhnika poluprovodnikov*, No. 1, 1968.

A^3B^5 COMPOUNDS

Mashukov and others[13] have studied the optical properties of strongly doped epitaxial n-GaAs films near their plasma resonance, on the basis of infrared reflection and absorption. Electron concentrations were on the order of 6-9 x 10^{18} cm^{-3} and film thickness varied from .5 μ to 17 μ. The films' spectra revealed an interference pattern superimposed on the plasma pattern as a result of reflections from the film-substrate interface. Experimentally derived equations governing reflections from extremely thin films (0.5 μ) revealed a very washed-out plasma pattern. Theoretical computations were used to show that, as film thickness approached zero, the plasma pattern not only washed out but the plasma minimum shifted toward the shortwave side. Spectral analysis showed that the real component of the dielectric constant varied according to the Drude model, while its imaginary component increased (with increasing wavelengths) at a more rapid rate.

Mashukov and Kravchenko[14] investigated the Faraday effect in strongly doped epitaxial films of GaAs. The films (0.5-17 μ thick) were obtained by liquid epitaxy from molten tin on substrates of polarized GaAs. The authors determined the Faraday effect near plasma frequencies using Drude's conditions for optical constants of a doped semiconductor in a longitudinal magnetic field, with a few assumptions.

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[13] Yu. P. Mashukov, A. F. Kravchenko, and Yu. B. Bolkhovityanov, "Optical Properties of Doped Epitaxial GaAs Films near Plasma Resonance," *Fizikia i tekhnika poluprovodnikov,* Vol. 5, No. 9, 1971.

[14] Yu. P. Mashukov and A. F. Kravchenko, "Faraday Effect in Doped Epitaxial GaAs Films," *Fizika i tekhnika poluprovodnikov,* Vol. 6, No. 1, 1972.

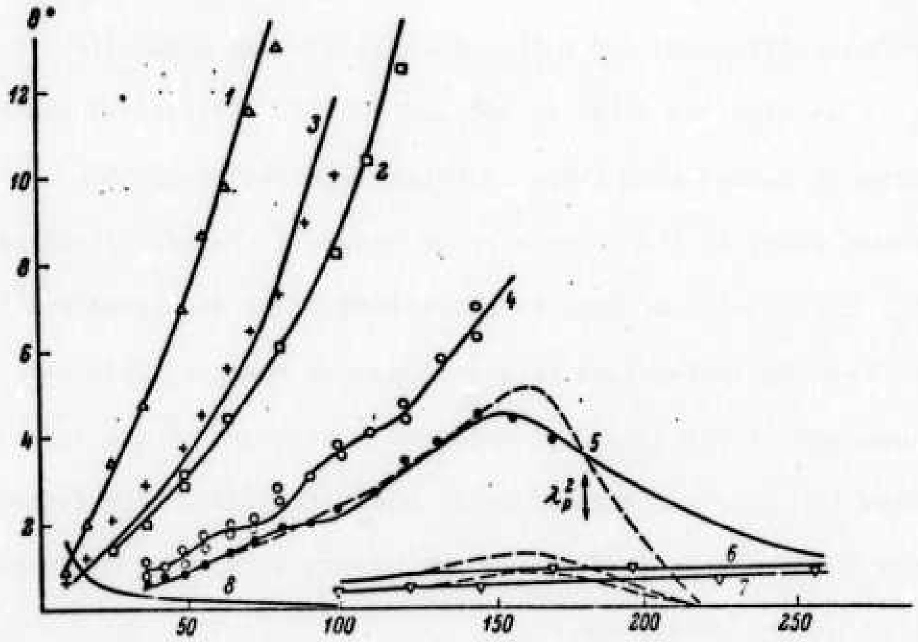

Fig. 20 - Faraday effect in strongly doped GaAs films.
1 - 15-17 μ film thickness; 2 - 7.2 μ film thickness; 3 - 6 μ film thickness; 4 - 3.4 μ film thickness; 5 - 2.4 μ film thickness; 6 - 0.6 μ film thickness; 7 - 0.4 μ film thickness; 8 - 1.15 mm-thick substrate; λ_p^2 - spectral position of the square of the plasma wavelength for curves 5-7.

Dashed lines in Fig. 20 represent the simple Faraday effect thus computed. The solid lines in the graph represent the full Faraday effect derived experimentally.

A^5B^6 COMPOUNDS

Ivkin and others[15] derived the relation of high-frequency conductivity (100-2000 kHz) in As_2Se_3 and $As_2Se_3 \cdot As_2Te_3$ to hydrostatic pressure. They described the conductivity mechanism in detail.

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[15] E. B. Ivkin, B. T. Kolomiets, E. M. Raspopova, and K. D. Tsendin, "Effect of Pressure on the High-Frequency Conductivity of Chalcogenide Glass," *Fizika i tekhnika poluprovodnikov*, Vol. 5, No. 9, 1971.

Kolomiets and others[16] experimentally studied variations in the absorption coefficient and index of refraction in glass-like films of As_2Se_3 in an electric field at 300 and 160° K. Electrical-absorption measurements agreed with those expected from the Franz theory and showed that, in the absence of an external electric field and with $\hbar\nu < E_g$, the absorption edge is characterized by an exponential relation of the absorption coefficient to photon energy. This conclusion was supported by the nature of recorded variations of the index of refraction when the film was exposed to an electric field. The deviation from the Franz theory centered on the observed relation of temperature to shifts in the absorption edge.

ANOMALOUS-PHOTOVOLTAGE EFFECT IN FILMS

Arifov and others[17] examined the influence of ion bombardment on the photoelectric properties of Si and Ge films exhibiting anomalous photovoltages. They found that bombardment of these films with alkali ions led to significant changes in the generated photovoltages, and in resistivity. Thick films exposed to ion irradiation of 50-3000 ev registered a decrease in the generated photovoltages, while thin films showed an increase. In both cases, film resistivity decreased. Small-dose bombardment of the same films with ions of greater energy than 3 kev resulted in the total disappearance of the generated photovoltage (in both cases), accompanied by a sharp drop in resistivity.

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[16] B. T. Kolomiets, T. F. Mazets, Sh. Sh. Sarsembinov, and Sh. M. Efendiev, "Variation of Optical Properties in Glass-Like As_2Se_3 Layers under the Influence of an Electric Field," *Fizikia i tekhnika poluprovodnikov,* Vol. 5, No. 12, 1971.

[17] U. A. Arifov, N. Abullaev, and A. Kh. Ayukhanov, "Effect of Ion Bombardment on Photoelectric Properties of Si and Ge Films Generating High Photovoltages," *Fizika tverdogo tela,* Vol. 12, No. 7, 1970/

Korsunskiy and others[18] investigated the photomagnetic effect (PME) in CdTe films exhibiting an anomalous photovoltage (APV) effect. The .03 to 1.6 μ-thick CdTe films were obtained by thermal evaporation on substrates of polished fuzed-quartz (10 x 20 mm). The table presented below shows the measured short-circuit current (1×10^{12} amp) for nine samples irradiated with white light of 10^4 lux intensity.

Table 3

SHORT-CIRCUIT CURRENT IN CdTe FILMS

Film Thickness (μ)	Direction of Irradiation			
	Frontal		Rear	
	$i_{APV} \times 10^{12}$ amp	$i_{PME} \times 10^{12}$ amp	$i_{APV} \times 10^{12}$ amp	$i_{PME} \times 10^{12}$ amp
0.03	- 3	- 0.3	- 5.6	- 0.05
0.11	+280	+ 50	+360	+ 15
0.14	- 52	0	- 34	- 2
0.21	-125	- 1	-105	- 1
0.25	+690	+ 60	+560	+ 10
0.27	- 86	+ 7	+ 26	- 4
0.28	- 44	+ 9	+ 15.5	- 4
0.73	+ 42	+ 13	- 34	- 14
1.60	+1330	+100	+1000	-200

18 M. I. Korsunskiy, M. N. Sominskiy and V. N. Smurygin, "Photomagnetic Effect in CaTe Films Exhibiting Anomalous Photovoltages," *Doklady AN SSSR*, Vol. 203, No. 2, 1972.

Uskov and Petrov[19] studied the anomalous photovoltage (APV) effect in lead iodide. The 0.1-0.2 μ-thick films were obtained by vacuum deposition (10^{-5} torr) on mica substrates (20 x 10 mm) at room temperature. The angle of deposition was 30° and the rate was 15-30 Å/sec. Table 4 and Figs. 21, 22, and 23 show the findings of this study.

Table 4

APV IN LEAD IODIDE FILMS

Sample No.	V_{apv}(v)	I(10^{12} amp)	R_{dark}(ohm)
4	45	2.5	10^{14}
7	57	7.5	$1.6\cdot10^{14}$
9	40	2.7	$5\cdot10^{13}$
11	34	2.3	$2.5\cdot10^{14}$
14	54	6.3	$2.4\cdot10^{14}$
20	—78	6.0	$1.2\cdot10^{14}$

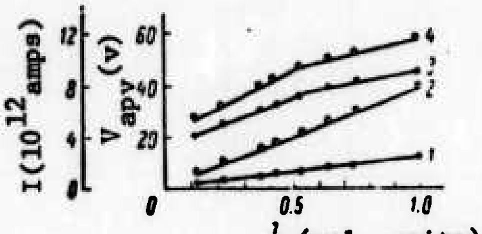

Fig. 21 - Variation of APV with irradiation.
Maximum intensity was 0.7 x 10^{-3} ω/cm^2, λ = 490 nm.
1 & 2 - Short-circuit photocurrent; 3 & 4 - photovoltages;
1 & 3 - sample 4 (see Table 4); 2 & 4 - sample 7 (see Table 4).

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[19] E. M. Uskov and V. P. Petrov, "Effect of Anomalous Photovoltages in Lead Iodide Films," *Fizika i tekhnika poluprovodnikov*, Vol. 5, No. 11, 1971.

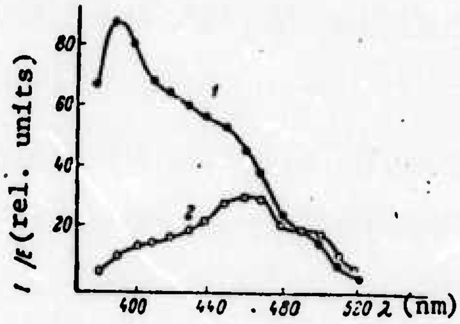

Fig. 22 - Spectral distribution of short-circuit photocurrent. 1 - Frontal irradiation; 2 - irradiation from the rear.

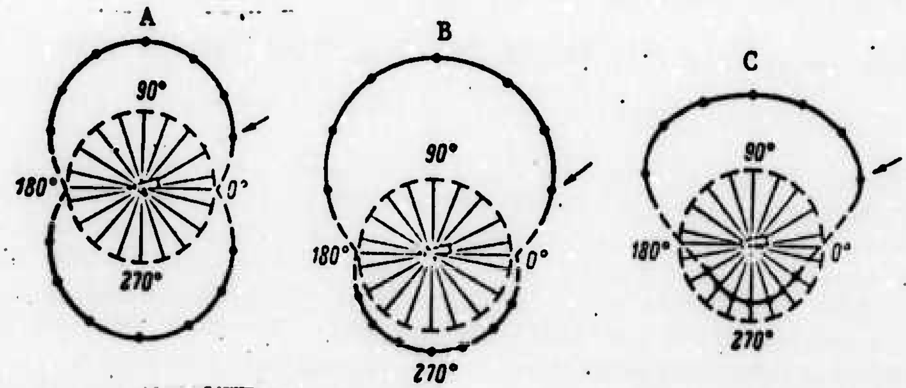

Fig. 23 - Variation of V_{APV} with angle of irradiation. A - Irradiation with λ = 490 nm; B - irradiation with λ = 140 nm; C - irradiation with λ = 320 nm.

Igras and Orlowski[20] presented a general discussion of observed anomalous photovoltages in thin films of Si, Ge, CdTe, CdSe, and $Cd_xHg_{1-x}Te$. In each case, the films were obtained by vacuum evaporation on a heated substrate (20-800° C). White light was the main source of film irradiation. The authors note that many published experiments show that traps have a highly influential role in the phenomenon -- i.e., a parallelism can be noticed between photovoltage characteristics and trap behaviors. The APV properties of the various films are enumerated.

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[20] E. Igras and B. Orlowski, "Anomalous Photovoltages in Semiconductor Films," *Proceedings of the Second Colloquium on Thin Films*, Akademiai Kiado, Budapest, 1967.

VIII. QUANTUM-SIZE AND SPACE EFFECTS

Tavger and Demikhovskiy[1] have been doing considerable work on quantum-size effects. According to them Soviet interest in the study of the quantization of quasiparticles in films has increased in connection with the extensive utilization of thin semiconductor films in microelectronics. The interest in semiconductor films stems from the fact that they exhibit size quantization effects that are more pronounced and take place in greater film thickness ($\sim 10^{-5}$ cm) than in metals.

OVERVIEW

Quantization of the transverse motion in films can appear only if certain conditions are satisfied. Because of electron scattering, the quasidiscrete spectrum partially washes out. In order for the quasidiscrete nature of the spectrum to be maintained, it is necessary that the broadening h/τ(τ -- relaxation time) be smaller than the distance between the neighboring subbands:[2]

$$\frac{\hbar}{\tau} \ll \varepsilon_{s+1} - \varepsilon_s \ .$$

For an exact determination of τ it would be necessary to calculate the damping of the quasiparticles in the film for different possible scatter-

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[1] B. A. Tavger and V. Ya. Demikhovskiy, "Quantum-Size Effects in Semiconductor and Semimetal Films," *Uspekhi fizicheskikh nauk*, Vol. 96, No. 1, 1968.

[2] Quasiparticle energy (in a film) is determined by the longitudinal projections of the quasimomentum $\bar{k}$ (both x and y components) and by a discrete quantum number s (which replaces the z component). At a fixed s, the energy is continuous through an interval of values which the Soviets refer to as a subband.

ing mechanisms, as was done by Rytova for electron-electron and electron-impurity scattering.[3] Since it is impossible to obtain a sufficiently accurate theoretical estimate, it is necessary to determine the relaxation time experimentally. For estimating purposes, it can be expressed in terms of the experimentally measured mobility. This means that the transport relaxation time, which takes into account all the carrier-scattering mechanisms in the film, is substituted in the above relation.[4]

Quantum-size effects in semiconducting films are not identical with those in semimetallic films. In the latter, as a rule, the charge carriers are degenerate, and oscillatory effects, therefore, are pronounced. In semiconductors, on the other hand, in order for oscillatory effects to be observable, a high doping level is necessary, which leads to decreased carrier mobility. However, the large variety of semiconducting materials makes it possible to choose a film with better parameters than those of a semimetal.[5]

U. S. researchers, Crittenden and Hoffman, observed certain deviations in electrical resistivity of thin nickel films from the values predicted by the classical theory. They ascribed the deviations to the influence of electron-energy quantization. They assumed that the presence of quantization leads to a decrease in the number of possible

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[3] N. S. Rytova, "Damping of Quasiparticles in Electron-Electron Scattering," *Doklady AN SSSR*, Vol. 163, 1965; and "Quasiparticle Damping for Electron-Impurity Scattering," *Fizika tverdogo tela*, No. 8, 1966.

[4] Tavger and Demikhovskiy, "Quantum-Size Effects. . . ," op. cit.

[5] Ibid.

transitions, since only discrete values of the transverse momentum are allowed in the film. This causes a decrease in resistivity (compared with classical theory) with decreasing film thickness. However, Tavger and Demikhovskiy argue that this explanation of the peculiarities of the experiment is not valid, since quantization cannot lead to a monotonic decrease in resistivity with decreasing thickness. They state that the first convincing experimental confirmation of the presence of a quasi-discrete electron spectrum was obtained in thin semimetallic films. Ogrin[6] and other Soviet researchers observed oscillations in the mobility, in the Hall constant, and in magnetoresistance in Bi films as a function of film thickness.

A direct observation of the quantization of the motion of electrons was carried out by Lutskiy and others[7] in experiments on the tunneling effect between thin films.

The quantization of transverse electron motion was observed by Komnik and Bukhshtab in antimony.[8] They observed oscillations of resistivity with varying thickness in the ~ 100-400 Å range. Instead of using a set of films of varying thickness, they used a sample in the form of a wedge, thus increasing the accuracy with which the film thickness could be determined.

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[6] Yu. F. Ogrin, "Properties of Bi Films," *Zhurnal eksperimental'noy i teoreticheskoy fiziki (Pisma)*, No. 3, 1966.

[7] V. N. Lutskiy, D. N. Korneev, and M. I. Elinson, "Quantization of Electron Motion," *Zhurnal eksperimental'noy i teoreticheskoy fiziki (Pisma)*, No. 4, 1966.

[8] F. F. Komnik and E. I. Bukhshtab, "Quantization of Transverse Electron Motion," *Zhurnal eksperimental'noy i teoreticheskoy fiziki (Pisma)*, No. 6, 1967.

Soviet researchers have noted that effects analogous to quantum-size effects in films can occur in the thin surface layer of a bulky sample when the energy bands are sufficiently deflected. Just as in a film, the deflection of the bands limits the carrier motion normal to the sample surface. As a result, when a number of conditions are satisfied, the carrier spectrum becomes quasidiscrete -- $\varepsilon = \varepsilon(k_x, k_y, s)$. In the case of many-valley single-crystals, just as in a film, splitting of energy levels is possible and can lead to a decrease in the number of equivalent valleys.[9]

The surface deflection of the bands can be varied by means of an external electric field applied normal to the sample surface. In some sense, a change in the magnitude of the field is analogous to a change in film thickness, and can lead to similar effects. An appreciable number of papers devoted to quantization in the surface layer have been published. Oscillations of the magnetoresistance have been observed in the surface layer in a quantizing magnetic field.[10]

The field effect can be used in principle to study the properties of films with a quantized spectrum. This method, proposed by Sandomirskiy,[11] consists of the following: The investigated film serves

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[9] Tavger and Demikhovskiy, op. cit.

[10] Ibid.

[11] V. B. Sandomirskiy, "Field Effect in Films with a Quantized Spectrum," *Zhurnal eksperimental'noy i teoreticheskoy fiziki*, Vol. 52, 1967.

as one of the plates of a capacitor. By varying the potential difference it is possible to vary the electron concentration in the film in such a way that the number of filled subbands varies. This can lead to an oscillatory dependence of the mobility and conductivity on the voltage applied to the capacitor. One way of varying the carrier concentration in the film is to subject the film to pressure.

An experimental study of this effect on Bi films[12] has shown that the oscillations actually take place in the ~2000-3000 Å thickness interval. However, it is impossible to present an exact interpretation of the results obtained by assuming that the transverse field leads only to a change of carrier concentration. At small thicknesses, the penetration of the field into the film becomes important, and this should lead to a change of the energy spectrum in the film. This makes accurate analysis of the field effect in the film very difficult.

The number of quantum-size effects is not confined to the specific dependence of the kinematic and thermodynamic characteristics on film thickness. Quantization of motion also leads to a change in the temperature dependence of the film properties and to a new dependence of these properties on the magnitude and direction of the magnetic and electric fields. The quasidiscrete character of the spectrum leads to different resonance phenomena when electromagnetic radiation, sound, and electron current pass through the film.[13]

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[12] Yu. F. Ogrin, V. N. Lutskiy, and M. I. Elinson, "Field Effect in Bi Films," *Fizika tverdogo tela*, No. 9, 1967.

[13] Tavger and Demikhovskiy, op. cit.

If a thin film is placed in a magnetic field, the quantization of electron motion will be due both to the limited size of the sample and to the presence of Landau levels. In a transverse field, the transverse motion is independently quantized as a result of the limited size of the film, and the longitudinal motion is quantized as a result of the presence of the magnetic field. Hence the spectrum becomes purely discrete, and the energy levels are produced as a result of superposition of film levels and Landau levels. On the other hand, in the case of a longitudinal field it is impossible to separate the influence of the limited transverse dimensions of the film and of the magnetic field. As a consequence of the joint action of these factors, the transverse motion of electrons becomes quantized, and the longitudinal motion remains quasiclassical as before, but an anisotropy of the effective masses arises.[14]

Thus, when a magnetic field is superimposed on a film, the spectrum becomes discrete or quasidiscrete. This must also lead to oscillations in the kinematic and thermodynamic quantities. However, oscillations are possible whether it is the film thickness or the field that changes.[15]

RECENT RESEARCH

Blokh and others[16] recently investigated quantum-size oscillations in films during inelastic scattering of electrons by high-frequency

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[14] Ibid.

[15] Ibid.

[16] M. D. Blokh, V. A. Margulis, and B. A. Tavger, "Quantum-Size Oscillations of Kinetic Coefficients in Films during Inelastic Scattering of Electrons by High-Frequency Phonons," *Fizika i tekhnika poluprovodnikov,* Vol. 5, No. 8, 1971.

phonons. They determined the coefficients of electron conductivity, thermoconductivity, and thermal emf in effect during the interaction of charge carriers with phonons in films exhibiting quantum-size phenomena. They showed that films exhibit anomalies at thicknesses where the film level coincides with the energy of an excited electron. These anomalies manifest themselves via oscillations in the kinetic coefficients or, at least, in their derivatives (with changes in film thickness). A period of oscillation was observed that was governed by the frequency of the optical phonons (ω_0) and that differed from previously observed oscillations related to elastic scattering.

The oscillations were observed in InSb at room temperature, where inelastic scattering is insignificant. For this reason, the observed oscillation period was determined by the population of the energy subbands. At low temperatures, where interactions with optical phonons are essentially inelastic, a second oscillation period (shorter than the first) sometimes arises in semiconductor films of the InSb type. Also, unlike the case of elastic scattering, the cited oscillations do not disappear in the pure-semiconductor case, where the electronic gas is nondegenerate. The effect according to Blokh and his associates, is most noticeable in thin films (< 500 Å).

Genkin and others[17] have studied nonlinear susceptibility in size-quantized films. Current, arising under the influence of a field

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[17] V. N. Genkin, Yu. A. Romanov, and V. V. Sokolov, "Nonlinear Susceptibility of Size-Quantizing Films," *Fizika tverdogo tela*, Vol. 13, No. 8, 1971.

E, was found to be a nonlinear function of E in fields where

$$E \sim \hbar^2 / emd^3,$$

where d represents film thickness and m is the effective mass of free carriers. A tripling effect -- a product of size quantization -- was observed in InSb films placed in the reflection plane of a flat dielectric waveguide. An InSb film ($d = 3 \times 10^{-6}$ cm, $n = 5 \times 10^{17}$ cm^{-3}, and $S = 1$ cm^2) placed in a mica ($\varepsilon \sim 5$) waveguide (1 x .005 cm/in cross-section) increased the frequency of the 10^{-12} rad sec^{-1} (20 watt) signal being input to the waveguide to 3×10^{-12} rad sec^{-1} (20 μ watt).

Volkov and Pinsker[18] examined selected aspects of the quantum-size effect in films of variable thickness. They showed that carriers are incapable of penetrating the sharp edge of a wedge-shaped film beyond the point where wedge thickness approaches the de Broglie wavelength. Voltampere characteristics of the interface of a metal-wedge-shaped film were analyzed, as were anti-Stokes emissions from a wedge-shaped film. In conclusion, Volkov and Pinsker observed that size-quantized films of a periodically variable thickness (in one dimension) are superstructural.

Romanov[19] has been working on cyclotron resonance in size-quantized semiconductor films with electron scattering by acoustic phonons and their reflection from film boundaries. He has found that the

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[18] V. A. Volkov and T. N. Pinsker, "Quantum-Size Effect in Films of Variable Thickness," *Fizika tverdogo tela,* Vol. 13, No. 5, 1971.

[19] A. A. Romanov, "Cyclotron Resonance of Thin Films," *Fizika i tekhnika poluprovodnikov,* Vol. 5, No. 2, 1971.

halfwidth of the observed cyclotron absorption line is a function of film thickness.

Vysokoostrovskaya[20] has performed a theoretical study of the effect of a one-dimensional deformation on the electric resistance in semimetallic films exhibiting quantum-size effects. She has found that deformations lead to an energy shift in charge carriers in k-space proportional to the deformation, and further that resistance is a discontinuous function of deformation parameters and film thickness.

Chaplik and Entin[21] have investigated charged impurities in very thin films. They show that ionized impurities in films of thicknesses less than the effective Bohr electron radius lead to the appearance of quasistationary energy levels. Also, donor activation energy increases significantly, in comparison to its bulk value. And the relation of temperature to electron mobility differs from that found in large samples. Electron mobility was found to be a function of $T^{1/2}$ at low temperatures (instead of $T^{3/2}$).

Kazaryan and Enfiadzhyan[22] have studied the importance of exciton effects on the coefficient of interband light absorption $\alpha(\omega)$ in semiconductor films exhibiting quantum-size effects. The investigated films -- e.g., InSb -- had large dielectric constants ε and small effective charge-carrier mass. Figure 24 illustrates the qualitative behavior of the interband absorption coefficient.

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[20] N. A. Vysokoostrovskaya, "Effect of Deformation on Quantized Semimetal Films," *Uchenye zapiski Gorkovskogo universiteta: Seriya fizicheskaya,* No. 126, 1971.

[21] A. V. Chaplik and M. V. Entin, "Charged Impurities in Super Thin Films," *Zhurnal eksperimental'noy i teoritcheskoy fiziki,* No. 6, 1971.

[22] E. N. Kazaryan and R. L. Enfiadzhyan, "On the Theory of Light Absorption in Thin Semiconductor Films Exhibiting Quantum-Size Effects," *Fizika i tekhnika poluprovodnikov,* Vol. 5, No. 10, 1971.

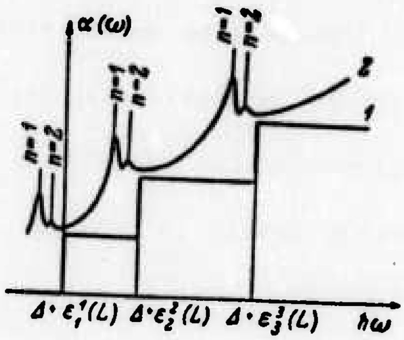

Fig. 24 - Variations in the interband absorption coefficient.

1 - Coulomb effect excluded;
2 - Coulomb effect included.

Blokh[23] did a study on the thermoconductivity of semimetal films exhibiting quantum-size effects. Using the matrix-density method (Wigner's concept), he determined current density and the density of heat flux for electrons (hole spectra were considered as nonquantized) in semimetallic films. He then examined phonon-scattering of charge carriers and computed thermoconductivity (taking into consideration two types of carriers and anisotropy). Finally, he analyzed the Wiedemann-Franz law and showed that the Lorentz number is basically a function of film thickness.

QUANTUM-SPACE EFFECTS

Nedorezov[24] examined spatial quantizing effects in semiconductor films, particularly Si and Ge films. He delved into three related areas: spatial quantizing in the case of a degenerate band, energy spectra of p-type Si and Ge films, and structural anomalies of the energy spectra and electron densities. Nedorezov showed that

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[23] M. D. Blokh, "Thermoconductivity in Semimetal Films Exhibiting Quantum-Size Effects," *Fizika tverdogo tela,* Vol. 12, No. 7, 1970.

[24] S. S. Nedorezov, "Space Quantization in Semiconductor Films," *Fizika tverdogo tela,* Vol. 12, No. 8, 1970.

electronic states arise in Si and Ge valence bands as a consequence of spatial quantizing, and that the uppermost subband (the one closest to the edge of the valence band) has saddle points, necessitating the introduction of logarithmic conditions into computations. He also presented a method for computing quantized energy levels in subbands on the basis of known band structure in bulk samples. The technique was said to be applicable to all semiconductor films with thicknesses >> a (where a is the interaction distance).

IX. DEVICES AND APPLICATIONS

Kemarskiy and others[1] are studying current oscillations generated in epitaxial GaAs films exposed to a pulsed field exceeding the critical value required for Rayleigh-wave amplification (at temperatures of 10 - 70° K). They have found that the observed current instability is associated with Rayleigh-wave amplification, which leads to the formation of acoustic-electric domains. The velocity of these domains -- determined by the period of oscillation -- is close to that of Rayleigh waves but less than the velocity of acoustic shear waves in GaAs. The appearance of current instability is accompanied by a change in the slope of the voltampere characteristics. When the field's pulse duration is increased, the current oscillation is damped. This phenomenon is attributed to the formation of a stationary domain at the anode.

Lyubov and Plakhotnik[2] are primarily interested in thin-film doping and related phenomena. However, the film preparation technique they describe would reportedly be invaluable in the preparation of integrated circuits, where it is imperative to know the form of the function describing the distribution of impurities along the vertical (z) axis of an epitaxial layer. Films with inhomogeneous distributions are said to be theoretically possible and desirable. Lyubov and Plakhotnik's calculation technique (when film growth as a function of

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[1] V. A. Kemarskiy, A. M. Kmita, and V. E. Lyubchenko, "Current Oscillations in GaAs Films when Subjected to Ultrasonic Rayleigh Wave Amplification," *Fizika i tekhnika poluprovodnikov*, Vol. 5, No. 7, 1971.

[2] B. Ya. Lyubov and V. T. Plakhotnik, "Calculation of the Impurity Distribution in an Epitaxial Film," *Kristallografiya*, Vol. 16, No. 5, 1971.

time is known) is supposed to generate the function describing the distribution of impurities entering the film from the substrate.

DETECTORS

Arifov and Abdullaev[3] used the anomalous photovoltage effect observed in Si and Ge films to develop an X-ray detector. They showed that their thin-film detector can detect X-radiation of even low intensity in both air and vacuum. Si and Ge films irradiated with visible light generate high photovoltages. Irradiation with only X-ray does not generate photovoltages. Simultaneous irradiation with both visible light and X-radiation causes a noticeable reduction in the photovoltage generated by the visible light alone. The reduction was found to be a function of X-ray intensity and hardness.

PHOTOELEMENTS

Shapochanskaya and others[4] investigated the capacitance of thin Se-film switching elements (in the form of an Ag-Se-Aℓ sandwich) as a function of irradiation, alternating-voltage frequency and fixed bias. They determined the wavelengths of incident light capable of eliciting changes in bulk properties of irradiated specimens. A model of a two-layer capacitor was used to interpret the experimental results.

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[3] V. A. Arifov and N. Abdullaev, "Using the Anomalous Photovoltage Effect in Si and Ge Films to Detect X-Radiation," *Pribory i tekhnika eksperimenta*, No. 2, 1972.

[4] Z. V. Shapochanskaya, S. I. Konyaev, and Kh. I. Klyaus, "Bulk Properties of Se Thin Film Switching Elements," *Fizika i tekhnika poluprovodnikov*, Vol. 4, No. 5, 1970.

Vlasenko and Savin[5] studied low-voltage electroluminescent ZnS-Cu, Cℓ films from the viewpoint of both their potential applications in various electroluminescent devices and their utilization as light sources in electronics (because of their low operating voltage and their blue-green luminescence). Electroluminescence was studied with the ZnS (2-2.5 μ-thick) in a sandwich-type structure. The ZnS film was placed between SnO_2 and Aℓ electrodes, with an SiO insulating layer (50 mm) between the film and the Aℓ electrode. The SiO film improved electric stability and increased the brightness of pre-breakdown luminescence. The researchers found that electroluminescence could be induced (in ZnS) only by an alternating field -- indicating the existence of charge polarization in these films.

Fedorov and Benderskiy[6] discussed the potential of magnesium phtalocyanin photoelements. They list the properties of this photoconductor and draw attention to the ease with which these properties can be advantageously altered through selective doping.

Chukova[7] published a lengthy study on the properties of electroluminescent ZnS-Cu capacitors, in which she enumerates in great detail all known ZnS-Cu properties.

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[5] N. A. Vlasenko and A. K. Savin, "Low-Voltage Electroluminescent ZnS-Cu,Cℓ Films," *Zhurnal prikladnoy spektroskopii*, Vol. 16, No. 1, 1972.

[6] M. I. Fedorov and V. A. Benderskiy, "Properties of Thin Film Magnesium Phtalocyanin Photoelements," *Fizika i tekhnika poluprovodnikov*, Vol. 4, No. 7, 1970.

[7] Yu. P. Chukova, "Properties of Electroluminescent ZnS-Cu Capacitors," *Trudy fizicheskogo instituta im. P. N. Lebedeva AN SSSR*, Vol. 37, 1966.

CONTACTS

Niskov and Kubetskiy[8] devised an algorithm for computing the transitional resistivity between a metal contact and a thin semiconductor film.

Gubanov and Davydov[9] studied the case of ohmic contacts on semiconductor films with thicknesses on the order of the Debye radius. They computed the contact potential in such a film and determined energy-band shifts for films of any thickness.

SANDWICH STRUCTURES

Stafeev and others[10] advocate the use of organic superthin films (membranes) in sandwiches of the type metal-dielectric (semiconductor)-metal (MSM). In the known MSM structures with N-type and S-type voltampere characteristics there is a wide variance in parameters due to structural imperfections in the films. This problem does not arise in natural cellular membranes, nor in their artificially synthesized models. These synthetic membranes likewise possess N-type voltampere characteristics (in the presence of various electrolytes). The authors suggest a method for preparing MSM structures using either $C_{27}H_{45}OH$ or $C_{16}H_{33}OH$ for the organic film. The relation of current and capacitance

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[8] V. Ya. Niskov and G. A. Kubetskiy, "Resistance of Ohmic Contacts on Thin Semiconductor Films," *Fizika i tekhnika poluprovodnikov*, Vol. 4, No. 9, 1970.

[9] A. I. Gubanov and S. Ya. Davydov, "Computing the Contact Potential in Thin Semiconductor Films," *Fizika i tekhnika poluprovodnikov*, Vol. 5, No. 2, 1971.

[10] V. I. Stafeev, V. V. Kuznetsova, V. P. Molchanov, S. S. Serov, V. V. Pospelov, E. I. Karakushan, S. V. Ayrapetyants, and L. S. Gasanov, "Negative Resistance in Super Thin Organic Films between Metallic Electrodes," *Fizika i tekhnika poluprovodnikov*, No. 5, 1968.

to the applied voltage in an organic MSM is graphically presented in Fig. 25 below:

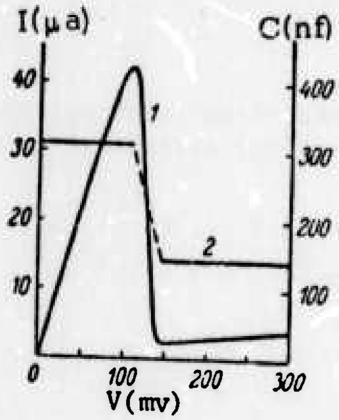

Fig. 25 - Variation of current and capacitance with applied voltage in MSM sandwiches.

1 - Current; 2 - capacitance

Baryshev and Gasanov[11] investigated the electric parameters of thin-film diode structures based on amorphous $A^2 - B^4 - C^5$ layers, particularly Cd-Ge-As. The films were 4-6 μ-thick. Sb, Bi, Cu, and Ni films were used as electrodes. Figures 26 to 29 show the findings of this study.

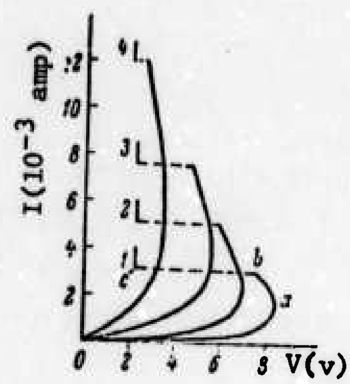

Fig. 26 - Direction-transition voltampere characteristics at room temperature

1 - S = .01 mm^2; 2 - S = .04 mm^2;

3 - S = .09 mm^2; 4 - S = .25 mm^2.

[11] V. G. Baryshev and L. S. Gasanov, "Electric Parameters of Thin Film Diode Structures Using Amorphous Layers of an $A^2 - B^4 - C^5$ Ternary System," *Fizika i tekhnika poluprovodnikov*, Vol. 5, No. 4, 1971.

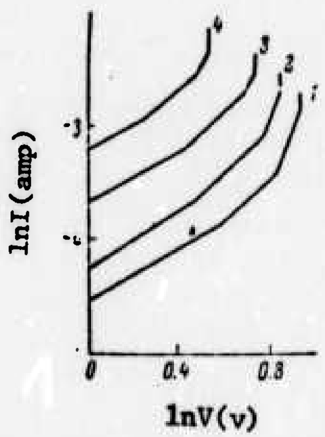

Fig. 27 - Direct-transition voltampere characteristics (closed-switch mode) up to V_B.

1 - S = .01 mm^2; 2 - S = .04 mm^2; 3 - S = .09 mm^2; 4 - S = .25 mm^2.

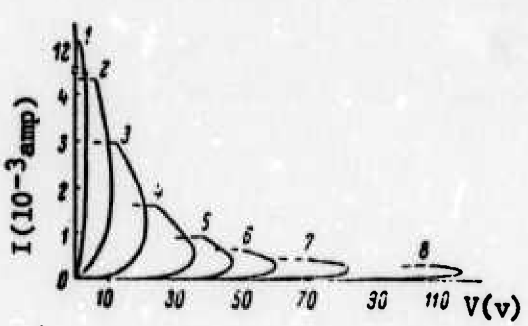

Fig. 28 - variation of voltampere characteristics with temperature

1 - 295° K; 2 - 259° K; 3 - 241° K; 4 - 227° K; 5 - 217° K; 6 - 209° K; 7 - 199° K; 8 - 179° K.

They generated surface acoustic waves in a piezoelectric epitaxial CdS film on a Ge substrate and analyzed the interaction of these waves with charge carriers in the substrate. At liquid nitrogen temperatures, they observed an increase in surface acoustic noise accompanied by increased intensity in acoustic-electric properties.

Kenigsberg and others[14] used .3-1.6 μ ZnO films to develop a hypersonic transducer. The film was prepared by vacuum evaporation onto the polished surfaces of sapphire, ruby, and/or other single-crystals, as well as of single-crystals with Ag, Aℓ, and Cu substrates. The ZnO film on a sapphire single-crystal without metallic substrate exhibited properties as given in Table 5

Table 5

PROPERTIES OF ZnO FILM ON SAPPHIRE

Film Thickness (μ)	ω(A/sec)	Resistivity (ohm cm)	Acoustic Loss (db per pass)
0.3	0.7-1.6	10^4	45
0.55	1.5	$2x10^4$	27
0.55	3	$2x10^4$	24
0.8	1.5	$3x10^4$	24
0.8	2.3	10^5	17
0.95	1.7	$3x10^4$	27
0.95	2.2	$4x10^4$	20
0.95	2.7	10^5	17
1.1	2.1-3.2	10^5	22
1.2	3.4	10^5	21
1.3	3.7	$3x10^4$	27
1.4	3.7	$3x10^4$	17
1.4	3.7	$3x10^4$	21
1.4	4	$5x10^4$	21
1.6	3.5-4.5	$2x10^4$	25

[14] N. L. Kenigsberg, A. N. Chernets, T. S. Kosmacheva, and A. A. Grinchenko, "Hypersonic Thin ZnO Film Transducers," *Fizika tverdogo tela,* Vol. 12, No. 6, 1970.

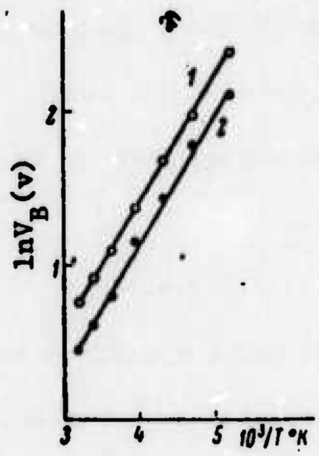

Fig. 29 - Variation of breakdown voltage with temperature.
1 - S = .01 mm^2;
2 - S = .25 mm^2.

In all the experiments presented in these four graphs, the Cd-Ge-As thin-film diodes had Sb electrodes, and the films were 4 μ thick.

Korzo and others[12] studied the electrical properties of various sandwich-type structures such as M-Ge, Si-$A\ell_2O_3$-M, and M-$A\ell_2O_3$-M. The $A\ell_2O_3$ films were 300-6000 Å thick. The researchers found that these particular structures exhibited negative N-type resistivity and were of a unipolar character.

ACOUSTIC ELEMENTS

Gulyaev and others[13] worked on the generation and amplification of surface acoustic waves in piezodielectric-semiconductor structures.

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[12] V. F. Korzo, L. A. Ryabova, and Ya. S. Savitskaya, "Conductivity of Thin Aluminum Oxide Films," *Fizika i tekhnika poluprovodnikov*, Vol. 2, No. 6, 1968.

[13] Yu. V. Gulyaev, A. M. Kmita, I. M. Kotelyanskiy, A. V. Medved, and Sh. S. Tursunov, "Generation and Amplification of Acoustic Surface Waves in a Piezodielectric Film - Semiconductor Structure," *Fizika i tekhnika poluprovodnikov*, Vol. 5, No. 1, 1971.

ELECTRO-OPTICAL DEVICES

Electro-optical devices under development are described in a paper by Men'shikh.[15] These are multimode devices that can be used as high-speed memory elements with large storage capacities in digital computers. One of the devices, the spectrotron,[16] uses a Fabry-Perot interferometer as the resonant circuit. The interferometer, controlled by an electric field, is illuminated with a parallel beam of monochromatic light with a spectral interval $\sum_{i=1}^{M} \nu_i$, having M lines distributed equidistantly with a spectral interval $\delta\nu$ greater than the interferometer transparency band. The interferometer is optically coupled to a photoelectric converter (a photoconductive cell or a photomultiplier), and loaded with a thin-film resistor which is connected to the conducting semitransparent coating on the interferometer surfaces. The operating speed of the device is determined by the relaxation constant of the photoelectric converter, and is on the order of 10^{-9} sec for photoelectric converters based on the photoemission effect.

Another multimode device described by Men'shikh, the synchro-spectrotron,[17] contains two Fabry-Perot interferometers (comprising an shf electro-optical modulator) which are synchronously tuned by an shf frequency-controlled oscillator and separated by an optical delay line with an external reflector. Input to one interferometer is illuminated with monochromatic light having a $\sum_{i=1}^{M} \nu$ spectrum, and the output from the

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[15] O. F. Men'shikh, "Electro-Optical Multimode Devices," *Radioelektronika*, Vol. 11, No. 9, 1968.

[16] O. F. Men'shikh, "Spectrotron," *Izobreteniya, promyshlennyye obraztsy, tovarnyye znaki*, No. 15, 1966.

[17] O. F. Men'shikh, "A Multimode Element: the Synchrospectrotron," *Izobreteniya, promyshlennyye obraztsy, tovarnyye znaki*, ibid.

second interferometer is optically coupled to a photoelectric converter whose integrating load is connected to the control input of an oscillator. Both interferometers have tuning ranges which allow them to be tuned to each spectral line of input light, so that a sequence of wave packets having ν_i frequencies (of the spectral lines) is formed at the output of the input interferometer, and pulse-modulated oscillations of the monochromatic light are formed at the output of the second interferometer under steady-state conditions.

Other, very similar devices are also described by Men'shikh.[18] They are not truly thin-film devices, but thin-film technology could easily be applied to their construction.

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[18] O. F. Men'shikh, "Synchrotron," *Izobreteniya, promyshlennyye obraztsy, tovarnyye znaki*, No. 19, 1966; "Pulse Counter with a Variable Scaling Factor," *Izobreteniya, promyshlennyye obraztsy, tovarnyye znaki*, No. 3, 1967; "Phasimnotron: a Phase-Pulse Multimode Element," *Izobreteniya, promyshlennyye obraztsy, tovarnyye znaki*, No. 12, 1967; "Electro-Optical Device with Multiple Stable States," *Izobreteniya, promyshlennyye obraztsy, tovarnyye znaki*, No. 13, 1966.

X. ANALYTICAL AND MEASUREMENT TECHNIQUES

Davydov and Chesnokov[1] describe wave attenuation techniques for computing the current flowing through a semiconductor film. They computed the probability of electron penetration through one- and two-layer film structures (taking crystal structure into consideration). Wave functions for the structure were calculated for the [100] direction. The coeff.cient of attenuation entering into the expression for current was approximated by a parabolic function.

Borman[2] believes that the best method of measuring the life time of inequilibrium charge carriers in epitaxial films is direct observation. Basically, the technique involves charge-carrier excitation with light when the film is "separated" from its substrate by a cutoff voltage.

Sladkov and others[3] describe a four-probe method they have used in determining the resistivity of epitaxial Si films. They cite the data they obtained using this technique.

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[1] S. Yu. Davydov and A. D. Chesnokov, "Electronic Wave Attenuation Method for Determining Current Flow in a Semiconductor Film," *Fizika i tekhnika poluprovodnikov*, Vol. 5, No. 11, 1971.

[2] D. V. Borman, "Method for Measuring the Life Time of Non-Equilibrium Charge Carriers in Epitaxial Films," *Fizika i tekhnika poluprovodnikov*, Vol. 6, No. 4, 1972.

[3] I. B. Sladkov, V. V. Tuchkevich, and N. M. Shmidt, "Errors in Determining Resistivity in Epitaxial Si Films Using the Four-Probe Method," *Fizika i tekhnika poluprovodnikov*, Vol. 5, No. 11, 1971.

INTERFEROMETRY

Gusev and others[4] present an interference method for measuring the effective thickness of ion-implanted films. The specimens used to demonstrate the technique were single-crystal Si and Ge films bombarded with P ions. The researchers derived formulas for computing the index of refraction and effective film thickness and compared their results with those obtained by etching methods. The results were within 10-15 percent of each other.

Meshcheryakov[5] demonstrates the use of a Jamin interferometer in the measurement of the film growth process. He believes the Jamin interferometer to be an invaluable tool in such studies.

SPECTRAL ANALYSIS

Streltsov and Khaybullin[6] described a method for measuring charge-carrier concentrations and mobility, as well as the conductivity and thickness of heavily doped, ion-implanted Si films, through analysis of reflection spectra near plasma resonance. Using that approach, they obtained values for n, μ, and the thickness (d) with a ±25% accuracy; σ was computed within ±30% accuracy.

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[4] V. M. Gusev, L. N. Streltsov, and I. B. Khaybullin, "Interference Method for Measuring the Effective Thickness of Ion-Implanted Films," *Fizika i tekhnika poluprovodnikov*, Vol. 5, No. 5, 1971.

[5] N. A. Meshcheryakov, "Incidence of a Shock Wave on the Surface of a Growing Si Film," *Fizika i tekhnika poluprovodnikov,* Vol. 5, No. 7, 1971.

[6] L. N. Streltsov and I. B. Khaybullin, "Calculation of Electrophysical Parameters of Strongly Doped Ion-Implanted Si Films from Their Reflection Spectra," ibid.

Rzhevskiy and Gribkovskiy[7] advocate using a spectral-luminescence approach to supplement other techniques -- e.g., electron microscopy, X-ray scattering, and infrared spectroscopy -- used in the structural analysis of inhomogeneous silicate glass. Rzhevskiy and Gribkovskiy believe their technique would provide additional structural information unobtainable by other methods.

Trilesnik[8] has made a lengthy study on using special-purpose multichannel spectrometers to automate the process of spectral analysis. He described in detail how such a system might be organized and how it would operate. However, such a system is not yet in existence. Trilesnik and others[9] have listed and discussed the currently available domestic photoelectric devices for spectral analysis.

DIFFRACTOMETRY

Shtremel[10] examined the limits of diffractometric analysis of thin-film structure. He evaluated various results obtained by diffraction techniques and determined the extent to which such techniques are capable of breaking down thin-film structure.

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[7] M. B. Rzhevskiy and V. P. Gribkovskiy, "Application of the Spectral-Luminescence Method to the Study of Inhomogeneous Si Glass Structures," *Zhurnal prikladnoy spektroskopii*, Vol. 16, No. 1, 1972.

[8] I. I. Trilesnik, "Automating Spectral Analysis Using Multichannel Photoelectric Devices," ibid.

[9] I. I. Trilesnik, S. V. Podmoshenskaya, S. A. Orlova, and N. S. Moskaleva, *Domestic Photoelectric Devices for Spectral Analysis and Development Trends*, Leningradskiy dom nauchno-tekhnicheskoy propagandy, Leningrad, 1969.

[10] M. A. Shtremel, "Limits of Diffractometric Analysis of Thin Structures, *Doklady AN SSSR*, Vol. 203, No. 3, 1972.

VISUAL MONITORING METHODS[11]

Most Soviet visual monitoring methods are based on determination of the films' thickness from its color. Observations are usually made with reflected light, for fluctuations in the transmission of the film-substrate system with increases in film thickness are not very significant in comparison to the average transmission value. The advantage of the visual monitoring method is its extreme simplicity. It has found wide application in the production of systems with few layers, especially antireflection coatings. When the visual method is used in the preparation of multilayer coatings, the thickness of each layer is monitored individually.

Reference instruments containing interference films of varying thickness have been proposed for improving control precision. During deposition, the film being monitored and the reference film are observed at the same angle at the point where the thickness of the latter has the desired value. Deposition is stopped at the moment when both films have the same color. By use of a reference wedge, a degree of control precision can be obtained that ensures a reflection coefficient error of no more than 0.05 percent in the deposition of a film that is antireflective in the 520 nm region. When standard references are not available, control is done with the aid of tables listing the films color-change sequence as its thickness grows. To monitor the thickness of

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[11] The information under the remaining three subheadings is based on L. B. Katsnel'son, "Methods of Controlling the Thickness of Vacuum-Deposited Films," *Optikomekhanicheskaya promyshlennost'*, No. 2, 1969.

colorless films, Soviet scientists have proposed a unique visual photometer, which employs the principle of converting ultraviolet radiation into three-color radiation that is made visible by luminescing compounds.

Measurements were made of the equal-thickness interference bands which appear in a wedge illuminated by monochromatic light with a wavelength λ_0 at those cross-sections where the optical thickness of the film forming the wedge is a multiple of $\lambda_0/2$. The wedge is formed by tilting the receiver with respect to the beam of evaporating material. By using this method simultaneously on three receivers tilted at different angles, 2-5 percent thickness control precision has been achieved.

PHOTOELECTRIC TECHNIQUES

A very widely used photoelectric method of monitoring film deposition is based on measuring the light passing through or reflected from the substrate onto which material is being vacuum-deposited. In this method, information on the film thickness is obtained from the known dependence of the transmission and reflection coefficients on the optical thickness. As shown in Fig. 30, a typical photoelectric apparatus used for this mounting method consists of a light source (1) -- an incandescent lamp -- located inside (or outside) the vacuum chamber (2); an optical system (3) that projects the light onto the item being monitored (the receiver), on which material is deposited from the evaporator (5) to form an optical coating on the receiver (4) and the film substrates (6); an optical system -- window (7), mirror (8), and lens (9) -- that directs the light that has passed through the receiver (or has been reflected from the receiver) onto a radiation detector; a selective

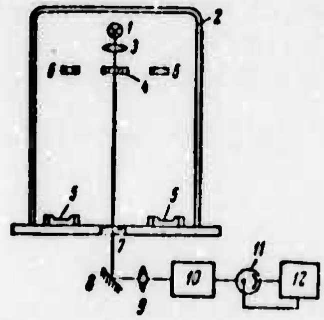

Fig. 30 - Basic layout of apparatus for monitoring optical thickness during deposition.

(1) light source; (2) vacuum chamber; (3), (7), (8), (9) elements of optical system; (4) receiver; (5) evaporators; (6) film substrates; (10) monochromatization system; (11) photodetector; (12) recorder.

optical instrument (10)-- light filter or monochromator -- that produces a beam with the desired spectral composition; a photoelectric detector (11); a photocurrent recording unit (12); and a power supply, not shown in Fig. 3C.

The monitoring is usually done with monochromatic light, by determining the instant when a transmission (or reflection) extremum is reached, indicating that the optical thickness nd is equal to $k\ \lambda_o/4$ ($k = 1, 2, \ldots$), where λ_o is the wavelength at which the monitoring is being done.

Direct monitoring by means of a single receiver is rendered difficult by the fact that, with an increase in the number of layers, the difference in the readings of the recording instrument, corresponding to successive maxima and minima, decreases. When monitoring is done in terms of the transmission coefficient T (T = 1-R), the sensitivity of the measuring circuit must be increased as the number of layers is increased. The most frequently used method for improving sensitivity involves increasing the light-source filament current on the photomultiplier power-supply voltage.

If monitoring is via reflection, then no more than four layers can be monitored directly. This shortcoming can be eliminated by means of compensation schemes, where the reading instrument is used to record the difference in the photo and compensation currents. The magnitude of the latter is selected in such a fashion that only that portion of the photocurrent caused by the buildup of the layer being measured remains uncompensated. The entire meter scale can be used to record the signal arising in this situation.

If a photodetector is used to record a dc signal, the measurements may be distorted by extraneous illumination, such as that generated by the incandescent evaporator. Moreover, in those cases where the photoelectric signal must be amplified and a photoresistor is used, it is undesirable to use a dc amplifier because of zero reading instability and a fluctuation level higher than that for an ac amplifier in the same passband. To eliminate these disadvantages, the luminous flux is modulated.

The moduiation is usually accomplished with a rotating disk with openings. The signal appearing at the photodetector is amplified by

an ac amplifier or by a selective amplifier, and is fed to the recorder after rectification. In most cases, a compensating device is employed in such amplifiers in order to permit use of the full scale.

In practice it has been shown that the effect of scattered light on the measurements can be eliminated without the use of modulation if light shields and baffles are properly arranged and the optical system elements are appropriately located with respect to the sources of stray light. The effect of scattered light is most effectively minimized when the desired wavelength is isolated with a monochromator having a small entrance opening and transmitting very few, if any, of the rays that strike the entrance slit at angles greater than that of the aperture. For dc operation without an amplifier the circuit is greatly simplified, increasing the reliability and excluding additional sources of error and noise.

Film-thickness control by way of the extremum technique is limited by the fact that in the vicinity of an extremum the reflection and transmission coefficients are almost invariable with thickness. This makes it difficult to ascertain the moment at which a film reaches the required thickness. In order to improve the sensitivity, a $\lambda_0/8$ layer can be deposited on the substrate beforehand. In this case, depositing a layer with an optical thickness of $k \lambda_0/4$ ($k = 1, 2, 3, \ldots$) onto the substrate produces a signal corresponding to a thickness equal to an odd multiple of $\lambda_0/8$. In this case a stronger dependence of the transmission (reflection) coefficient on thickness is observed than in the case of an extremum.

This method, however, requires that the output instrument be calibrated, which complicates the measurement, increases the stability

requirements, and introduces additional errors, both instrumental and those caused by the variance between the actual film refractive index values and those used for the calculation. Moreover, the error of the auxiliary layer is included in the final result.

Soviet scientists have described another monitoring method, not using the extremum. They propose monitoring at the computed wavelength λ, the reflection coefficient for which differs from that at the extremum by a factor of two. To avoid calibration, λ is obtained from the condition $\lambda < \lambda_0$. Then, during deposition, when the output signal reaches an extremum having a value that has been stored and is equal to the desired value, the deposition is terminated.

The nonextremum methods require that each layer be monitored on a separate receiver. In the preparation of multilayer films, this excludes the use of continuous monitoring, which, as mentioned above, can provide compensation for the error effects of the individual layers. Moreover, not only does the replacement of the receiver after the deposition of each layer complicate the equipment inside the bell jar, but it can also appreciably lower the precision with which an individual layer is deposited because of the difference in the condensation coefficient for deposition of a substance onto a clean receiver surface from that for deposition onto an already coated substrate. It has been shown that, in the preparation of a quarter-wave MgF_2 layer to be deposited on a ZnS film (or vice versa), the thickness will be 6-15 percent greater than for a layer deposited on a clean substrate being used for monitoring purposes.

The precision of determining the moment the required layer thickness is reached with the extremum monitoring method can be increased if a balanced method of recording is employed. The essence of one of the

possible balanced methods, termed the time-balance method, is as follows: during deposition the difference between the signals, proportioned to the transmission (reflection) coefficient at two instants of time, is recorded. A measurement cycle consists of storing the signals on condensers at one instant of time and then at another, and comparing the magnitudes of the stored signals. As one passes through an extremum, either the sign of the recorded difference signal changes, or the signal becomes zero.

Also proposed has been an apparatus containing two simultaneously operating photodetectors, one of which measures the radiant flux passing through the film being monitored, while the other measures the flux reflected from it. Lasers have begun to be used as light sources in photometric apparatus. It has been found to be impossible to obtain reflection coefficient measurements with better than 3 percent accuracy because of the poor stability of the laser radiation intensity. Gas-discharge lamps are sometimes used as sources of monochromatic radiation. Quarter-wave layers have been obtained with a precision of 4 percent by use of the 541.6 nm line of a mercury lamp. The Soviets have also attempted to use a low-voltage hydrogen lamp with an intense 121.6 nm line. An ionization chamber, sensitive in the 110-130 nm range (with a maximum at 121.6 nm), was used as the detector.

When lasers and gas-discharge spectral lamps are used, it is impossible to use the wavelength of the light for which the monitoring is to be done. Therefore, a radiator with a continuous spectrum (incandescent lamp) usually serves as the light source, and the wavelength λ_0, at which the monitoring is to be done, is isolated by means of a filter or monochromator. In cases where the transmission (reflection)

of the system of layers being deposited on the receiver varies little with the wavelength near λ_0, it is convenient to do the monochromatization with interference and absorption filters. By using a monochromator, one can deposit film while varying λ_0 during the film formation process. Another advantage of the monochromator is that, by controlling the spectral interval to be isolated, one can select the conditions for maximum sensitivity of the film-thickness monitoring system.

INTERFERENCE METHODS

Light interference determines the results of film-thickness measurement by any optical method. From this viewpoint all optical methods are interference methods. Nevertheless, the Soviet term "interference" designates only those methods which measure the location of the interference bands obtained when a special apparatus is used. These methods have found widest application for measuring the thicknesses of thin films, and at the present time are frequently used because of the high accuracy and reliability of the results obtained. Until recently, in spite of the merits of the interference method, it was rarely used for monitoring film thickness during deposition because of technical difficulties. The phenomenon of multiple-beam interference between two highly reflective surfaces has been used in monitoring the middle layer of a metal-dielectric filter. Two-beam interference has been used in measuring the thickness of a vacuum-deposited film. In one such apparatus a collimated light beam was incident on a plane mirror. The film to be studied was deposited on one half of the mirror; the second half was shielded from the material being deposited. Thus, two plane waves were reflected from the mirror, with the phase shift

between them being determined by the optical thickness of the film. The magnitude of the shift was measured by a polarization interferometer located outside the vacuum chamber. In spite of its high accuracy, the interference method has not found wide application, because it cannot be used for monitoring films deposited on a rotating substrate. Moreover, as the magnitude of the phase change at a metal-dielectric interface cannot be determined precisely, a special calibration is required each time.

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